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PREPARATION AND PROPERTIES OF THE SO-CALLED "NITROGEN IODIDE."

BY F. D. CHATTAWAY AND K. J. P. ORTON.

Nitrogen iodide was originally obtained by Courtois¹ in 1813 by the direct action of ammonia on solid iodine. Solutions of iodine in alcohol, chloroform, carbon tetrachloride, or aqueous potassium iodide were substituted for solid iodine by later observers, and both alcoholic and aqueous solutions of ammonia have been employed. In all cases a black or dark-brown amorphous solution was obtained.

Sérullas² prepared the substance by the interaction of iodine monochloride and a solution of ammonia, a method which was afterwards employed by Bunsen³. We have prepared nitrogen iodide by these various methods, and have compared the products which we find to be identical when proper precautions are taken to ensure the removal of all free iodine and ammonia and to prevent decomposition.

Whenever iodine itself is used, whether in solution or as a solid, less than half appears as nitrogen iodide. Exact experiments showed that at ordinary laboratory temperatures the nitrogen iodide formed contains about 47.5 per cent of the iodine used. Of the remainder 51.6 per cent appears as ammonium iodide and 0.8 per cent as ammonium iodate.

¹ Ann. Chim., **88**, 304.

² Ann. chim. phys. [2], **22**, 172 (1825); and **42**, 200 (1829).

³ Ann. Chem. (Liebig), **84**, 1 (1852).

The use of alcoholic solutions of iodine or ammonia decreases largely the yield because the nitrogen iodide reacts rapidly with the alcohol to form iodoform, which, moreover, can never be wholly removed from the product. Bunsen, however, used this method and obtained a substance, analysis of which led him to the formula $N_2H_4I_2$ for nitrogen iodide. All our analyses of nitrogen iodide prepared in various ways agree absolutely with this formula.¹

Preparation of Nitrogen Iodide by the Action of Iodine Monochloride on a Solution of Ammonia.

When iodine monochloride is used, 95 per cent of the iodine appears as nitrogen iodide. The remainder is converted into ammonium iodide and iodate, while the chlorine appears as ammonium chloride. We have carefully investigated this method and consider it the most suitable for preparing pure nitrogen iodide in large quantities. The best procedure for the preparation of the iodine monochloride and of the nitrogen iodide is as follows:

One hundred grams of finely powdered iodine are placed in 300 cc. of hydrochloric acid of sp. gr. 1.15 in a porcelain basin and 28 cc. of nitric acid of sp. gr. 1.41 are added. This quantity of nitric acid provides just sufficient chlorine to convert the iodine into iodine monochloride. The mixture is warmed on a water-bath to about 40° and continuously stirred, the beginning of the reaction being marked by the color of the liquid changing from brown to pale-yellow. The iodine gradually dissolves and the solution becomes orange in color. If the mixture be well stirred and the temperature not allowed to rise above 40°, no chlorine escapes. After the whole of the iodine has dissolved, the water in the bath is boiled for some time in order to expel the nitrosyl chloride. With the excess of hydrochloric acid used, the solution of iodine monochloride is perfectly stable and undergoes no decomposition even when boiled. To prepare nitrogen iodide it is cooled and diluted by adding about three times its bulk of crushed ice.

For every 10 grams of iodine 100 cc. of strong commercial

¹ Bunsen determines the relation of nitrogen to iodine only, and in his method of analysis any trace of iodoform present would not cause error.

ammonia (sp. gr. 0.880) are poured over about three times their weight of crushed ice and the cold solution of iodine monochloride slowly run in, the mixture being vigorously stirred during the addition.¹ The black precipitate of nitrogen iodide which at once separates, is filtered off by a pump through asbestos and washed with dilute ammonia, and finally, if required free from ammonia, three or four times with water. In this way a kilogram of nitrogen iodide can be obtained as a compact cake with perfect safety. It is best, if possible, to leave the solid mass damp with strong ammonia, for then filter-paper can be used instead of asbestos, and the slight decompositions which take place in the total absence of ammonia, and may give rise to local explosions, is prevented.²

Preparation of Crystalline Nitrogen Iodide.

In the course of this investigation it became obvious that nitrogen iodide is not formed by a direct substitution of iodine for hydrogen in ammonia, but that the iodine reacts with ammonium hydroxide as with other alkalies to form ammonium iodide and hypoiodite, and that the latter then decomposes, forming nitrogen iodide. This view was originally offered by Schönbein³ as a suggestion, which has been endorsed by Seliwanow.⁴ The addition of ammonia to an alkaline solution of potassium hypoiodite should, therefore, lead to the formation of NH_4OI , ammonium hypoiodite, which should then decompose, producing nitrogen iodide. This we have found to be the case; and, further, under certain conditions of concentration the nitrogen iodide separates in a crystalline form.

The following method gives good results: A decinormal solution of iodine monochloride is prepared by diluting with water to 1 liter a solution of iodine monochloride, ICl , made as above, from 12.7 grams of iodine. This dilute solution is

¹ The solution of ammonia should not be added to the solution of iodine monochloride, for then iodine is liberated and the yield much reduced.

² André (Jour. Pharm., **22**, 137 (1836)) obtained nitrogen iodide by the addition of ammonia to a solution of iodic acid in hydrochloric acid. Such a solution contains iodine monochloride after it has been heated, for, as is well known, iodic and hydrochloric acids then react according to the equation: $\text{HIO}_3 + 5\text{HCl} = \text{ICl} + 2\text{Cl}_2 + 3\text{H}_2\text{O}$.

³ J. prakt. Chem., **84**, 385 (1861).

⁴ Ber. d. chem. Ges., **27**, 1012 (1894).

unstable and should only be prepared immediately before use. Fifteen cc. of this solution are added to 100 cc. of a half-normal solution of potassium hydroxide (3 per cent), and then, as rapidly as possible, 10 cc. of ammonia (sp. gr. 0.880) are run in while the solution is gently shaken. The pale-yellow liquid remains clear for a short time, but within a minute glittering copper-colored crystals of nitrogen iodide begin to separate, and after a few minutes the crystallization is complete. The yield is satisfactory, being from 65-70 grams per 100 grams of iodine. When larger quantities than those indicated are used the yield is not so good owing to the difficulty of mixing the solutions sufficiently rapidly. Under the microscope very minute needles first become visible, which steadily grow to the usual crystals. The large excess of potassium hydroxide used prevents any setting free of iodine when the acid solution of iodine monochloride is added to it. If more than 15 cc. of $\frac{I_2}{10}$ be added to 100 cc. $\frac{KOH}{2}$, the crystals separate more rapidly and are smaller. With further increased concentration the crystals become mixed with amorphous nitrogen iodide, which finally forms the chief product.

Replacement of ammonia by a dilute solution of an ammonium salt also causes a deposition of crystalline nitrogen iodide, if the ammonium salt be added very cautiously. An amorphous precipitate is obtained if the solution of ammonium salt be added rapidly or if it be concentrated.

Amorphous nitrogen iodide can be converted into the crystalline variety by an apparent recrystallization from a hot solution of ammonia. The conversion is, however, really due to the occurrence of a reversible reaction in the system (nitrogen iodide + ammonium hypoiodite + ammonium hydroxide). In this system, at the state of equilibrium, the concentration of ammonium hypoiodite is greater at a high than at a low temperature with a given concentration of ammonia. To obtain crystalline nitrogen iodide by this method about 0.5 gram of the amorphous substance is heated with 100 cc. of thrice-normal ammonia solution, in which it partially dissolves, producing a pale-yellow solution, and this, after filtration through asbestos, deposits crystals when rapidly cooled. With larger quantities the time required to cool the bulk of hot liquid

leads to the conversion of so large a proportion of the ammonium hypiodite into iodate and iodide that little nitrogen iodide separates.

Crystals can also be obtained by the direct addition of a solution of iodine monochloride to ammonia. For this purpose the solution of ICl must be about one-fiftieth normal and must be added very slowly to a fairly concentrated solution of ammonia.¹

Properties of Nitrogen Iodide.

Crystals of nitrogen iodide suspended in water look like splinters of burnished copper, and when dry have a ruby-red color and a fine luster. Ordinary amorphous nitrogen iodide shows no trace of crystalline structure and appears quite black when suspended in water, but if filtered off and dried is seen somewhat to resemble the crystalline substance in color.

Pure nitrogen iodide is without effect on a neutral solution of litmus and gives no reaction of iodine when shaken with chloroform. In contact with water it soon shows signs of decomposition, the amorphous more rapidly than the crystalline variety. The crystals lose their lustre and under the microscope are seen to be etched and corroded. Too prolonged washing with water on the filter will cause this decomposition to take place. Free iodine is then always found by the chloroform test in the solid residue while free ammonia can be detected in the filtrate.²

Nitrogen iodide can be dried over lime or baryta in an atmosphere of ammonia, if light be absolutely excluded, without any decomposition taking place. When dry it can be safely detached from a porous tile with a spatula, but slight percussion, pressure between hard surfaces, or rapid heating

¹ The formation of nitrogen iodide has been observed in the action of bleaching powder on a solution of ammonium iodide. [Playfair in discussion on Gladstone's paper (Chem. Soc. J., 4, 34 (1852))]. In this case undoubtedly ammonium hypiodite is first produced and from it the nitrogen iodide is formed. The product separating is always mixed with calcium iodate, which can only with difficulty be removed by prolonged washing with ammonia. In the electrolysis of an ammoniacal solution of potassium iodide Losanitsch and Jowitschitsch (Ber. d. chem. Ges., 29, 2430) noticed that at the positive pole nitrogen iodide was deposited and that hypiodite could be recognized in the solution.

² Pure nitrogen iodide consequently cannot be obtained, as many observers have stated, by washing the product until the filtrate becomes neutral.

cause it to detonate with violence. The whole mass explodes at once without scattering, but the explosion is never communicated to any of the substance lying only a few centimeters away. A puff of violet vapor surrounded by a cloud of white fumes is seen, and in a dark room a green flash of light is noticed, resembling in color the flame of burning ammonia. Nitrogen iodide is remarkably sensitive to light. Bubbles of nitrogen are slowly given off in diffused light from the compound suspended in water while in direct sunlight rapid effervescence takes place. The dry substance in diffused light becomes gradually covered with minute crystals of iodine, which appear more quickly and grow more rapidly in sunlight.

Partially decomposed nitrogen iodide is very unstable and explodes at the slightest touch.

The following description of the crystals of nitrogen iodide has been given us by Mr. W. J. Pope, who very kindly undertook their examination: The crystals are small, flattened needles of a bright ruby color in transmitted light. The extinction through all faces in the zone of the long edge is straight and the crystals are probably orthorhombic; the forms would then be $\{001\}$, $\{101\}$ and $\{110\}$ and the crystals are lengthened in the direction of the axis b . The plane angle between the edges $001 : 101$ and $001 : 110$ is 140° and very frequently only one face of $\{110\}$ is present at one end. An optic axis can be sometimes just discerned at the edge of the field, emerging in the plane $\{010\}$.

The crystals are dichroic. On looking through $\{001\}$ using light polarized in the plane $\{100\}$ light of a beetle-green color is transmitted, but if the plane of polarization be $\{010\}$ light of a ruby-red color comes through.

The specific gravity of crystalline nitrogen iodide is about 3.5. This number has been obtained by drying a quantity of the substance in an atmosphere of ammonia in a specific gravity bottle and weighing it first in air and then under water.

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THE ACTION OF REDUCING AGENTS UPON NITROGEN IODIDE.

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All ordinary reducing agents when brought into contact with nitrogen iodide, suspended in water, rapidly decompose it. In these reactions the different reducing agents are invariably oxidized while hydriodic acid and ammonia are produced. The quantity of reducing agent oxidized is found in every case to be exactly double the amount equivalent to the hydriodic acid produced, using nitrogen iodide obtained by any method. The action of sodium sulphite, sulphurous acid, arsenious oxide, antimonious oxide, stannous chloride, and hydrogen sulphide has been investigated with the following results :

Amount of reducing agent oxidized	Na_2SO_3 , H_2SO_3 , As_2S_3 , Sb_2O_3 , SnCl_2 , H_2S					
Amount of hydriodic acid simultaneously produced	HI	HI	2HI	2HI	HI	HI

All the iodine contained in nitrogen iodide, therefore, behaves towards reducing agents like the chlorine contained in a hypochlorite and exerts twice its normal oxidizing action.

Action of Sodium Sulphite on Nitrogen Iodide.

When a solution of sodium sulphite in excess is added to nitrogen iodide suspended in water, rapid interaction ensues and a colorless solution, somewhat acid from the presence of hydriodic acid, results.

If the sulphite be added slowly from a burette a liquid colored brown by free iodine is obtained when the solid has entirely disappeared ; the end-point of the reaction is then easily seen by the disappearance of the color, or starch paste may be used as an indicator. The hydriodic acid produced can afterwards be estimated in one of several ways ; the most convenient and the one usually adopted is to titrate the clear solution with standard silver nitrate, using the blue so-called "iodide of starch" as indicator.¹ The actual operation is car-

¹ Pisani : *Annal. d. Min.*, 10, 83.

ried out as follows: Nitrogen iodide prepared in any one of the ways previously described is rapidly filtered off through asbestos by the aid of a pump, and thoroughly washed with decinormal ammonia, and finally once with water. A number of 250 cc. flasks having been prepared, about 0.2-0.5 gram of the moist iodide is placed in each with about 25 cc. of water, and titrated as rapidly as possible with decinormal sodium sulphite, shaking gently the while. The estimation of hydriodic acid by silver nitrate is then carried out in the ordinary way. Light must be rigorously excluded while washing and transferring the nitrogen iodide to the flask and during the titration until all solid particles have disappeared.

In the tables where the results are recorded the amount of reducing agent oxidized is stated in the second line, that of the hydriodic acid produced in the third, while in the fourth is the ratio between the reducing agent oxidized and the hydriodic acid produced, calculated to the third decinormal place.

The Roman numerals in the first column refer to the mode in which the nitrogen iodide used was prepared. The experiments numbered I were made with amorphous nitrogen iodide prepared by adding a decinormal solution of iodine in potassium iodide to a strong solution of ammonia; those marked II with material prepared similarly but using a normal solution of iodine. In those numbered III the nitrogen iodide was made by treating finely powdered iodine with a strong solution of ammonia; in those numbered IV iodine, precipitated by diluting a saturated solution of iodine in potassium iodide, was used. In preparing the material for those numbered V an alcoholic solution of iodine,¹ and for those marked VI a solution of iodine monochloride was added to a saturated solution of ammonia. In experiments VII and VIII crystalline nitrogen iodide was employed, prepared respectively by adding ammonium hydroxide to a solution of potassium hypoiodite and by heating amorphous nitrogen iodide with ammonia and rapidly cooling. In those numbered IX the nitrogen iodide was prepared by adding an excess of a solution of bleaching powder to a solution of ammonium iodide.

¹ In these cases a small residue of iodoform was left in the flask after titration.

Although in the tables one result only with each specimen of nitrogen iodide is given, this has in every case been confirmed by from 22 to 30 concordant experiments :

Number of experiment.	$\frac{N}{10} \frac{Na_2SO_3}{2}$ oxidized. cc.	$\frac{N}{10} HI$ produced. cc.	Ratio.
I	87.1	43.6	2 : 1.001
II	68.2	34.1	2 : 1
III	47.1	23.6	2 : 1.002
IV	70.5	35.3	2 : 1.001
V	86.2	43.2	2 : 1.002
VI	138.2	69.1	2 : 1
VII	60.8	30.4	2 : 1
VIII	98.1	49.1	2 : 1.001
IX	80.7	40.3	2 : 0.999

In order to establish beyond question this ratio between the sodium sulphite oxidized and the hydriodic acid produced, series of experiments have been made in which the latter was estimated by other methods.

In the following series, after the decomposition of sodium sulphite, the hydriodic acid was oxidized by iron-alum and sulphuric acid, and the liberated iodine distilled off and titrated by the same sulphite solution. The distillation was carried out in a special form of apparatus,¹ in which only ground glass joints are employed, and to prevent bumping, a very slow stream of carbon dioxide is led in by a capillary tube to the bottom of the boiling liquid :

Number of experiment.	$\frac{N}{10} \frac{Na_2SO_3}{2}$ oxidized by nitrogen iodide used. cc.	$\frac{N}{10} \frac{Na_2SO_3}{2}$ oxidized by iodine liberated from hydriodic acid produced. cc.	Ratio.
I	46	23	2 : 1
II	42.1	21.1	2 : 1.002
III	52.7	26.3	2 : 0.998
IV	65.6	32.7	2 : 0.997
V	45	22.5	2 : 1
VI	48.6	24.3	2 : 1

Exactly similar results were obtained when the hydriodic acid formed was estimated by adding an excess of silver nitrate

¹ Chem. News, 1899, 85.

and then determining the excess by a standard solution of potassium thiocyanate.

In connection with the action of reducing agents a number of experiments were made to show the necessity for the exclusion even of the diffused light of a laboratory when working with nitrogen iodide. Some amorphous nitrogen iodide prepared by adding a solution of iodine monochloride to ammonia was taken and carefully washed with decinormal ammonia. Approximately equal quantities were then placed in 4 flasks; that in flask *A* was titrated immediately with sodium sulphite; that in flask *B* was exposed to the diffused light of the laboratory on a dull winter afternoon for five minutes and then titrated; that in *C* was similarly exposed for ten minutes; that in *D* for twenty minutes. The hydriodic acid formed in each case was afterwards estimated by silver nitrate, and the ratio calculated between this and the sulphite oxidized.

Number of experiment.	$\frac{N}{10} \text{ Na}_2\text{SO}_3$	$\frac{N}{10} \text{ HI}$	Ratio.
	oxidized. cc.	present. cc.	
<i>A</i>	74.8	37.4	2 : 1
<i>B</i>	71.5	39.2	2 : 1.100
<i>C</i>	65	38.2	2 : 1.17
<i>D</i>	73.2	49.1	2 : 1.34

It is seen that the ratio diminishes as the time of exposure increases. This is due to a decomposition of some of the nitrogen iodide into nitrogen and hydriodic acid, a change which occurs whenever the substance is exposed to light.

A solution of sulphurous acid behaves toward nitrogen iodide as sodium sulphite does; a further action, however, accompanies this, similar to the one occurring when nitrogen iodide is exposed to light, whereby a small portion breaks up into nitrogen and hydriodic acid. This latter, as it is estimated with that produced by the reducing agent, causes the ratio to appear too low. If, however, the amount due to the reaction with the sulphurous acid be calculated from the ammonia formed, as can easily be done when the composition of the substance is known, the quantity of sulphurous acid oxidized is found to be exactly double that equivalent to the hydriodic acid produced.

Action of Arsenious Oxide on Nitrogen Iodide.

When a solution of arsenious oxide is slowly added to nitrogen iodide suspended in excess of a solution of sodium bicarbonate until the particles disappear, ammonia, arsenic acid, and hydriodic acid are produced, and the amount of arsenious acid oxidized is found to be exactly double that which is equivalent to the hydriodic acid formed. The experiments were carried out much as before, the hydriodic acid, however, being estimated by making the liquid acid, adding silver nitrate in slight excess, and estimating the excess added by potassium thiocyanate.

Number of experiment.	$\frac{N}{10} \text{ As}_2\text{O}_3$	$\frac{N}{10} \text{ HI}$	Ratio.
	oxidized. cc.	produced. cc.	
I	42.3	21.1	2 : 0.997
II	45.9	22.9	2 : 0.997
III	37.9	18.9	2 : 0.997
IV	44.5	22.3	2 : 1.002
VI	43.8	21.9	2 : 1
VII	33.2	16.6	2 : 1

Similar results were obtained when the hydriodic acid was estimated by determining the amount of a standard solution of potassium permanganate required to oxidize it to iodic acid.

Action of Antimonious Oxide on Nitrogen Iodide.

The action of antimonious oxide on nitrogen iodide is exactly similar to that of arsenious oxide, the compound being converted into the higher oxide, while ammonia and hydriodic acid are produced. Similarly the quantity oxidized is double the amount equivalent to the hydriodic acid formed. The experiments were carried out as with arsenious oxide, a decinormal solution of tartar emetic being used and sodium bicarbonate added in larger excess.

Number of experiment.	$\frac{N}{10} \text{ Sb}_2\text{O}_3$	$\frac{N}{10} \text{ HI}$	Ratio.
	oxidized. cc.	produced. cc.	
I	31.3	15.7	2 : 1.003
II	39.4	19.8	2 : 1.005
III	32.6	16.4	2 : 1.006
IV	26.1	13.1	2 : 1.003
VI	38.2	19.1	2 : 1
VII	34.7	17.4	2 : 1.002

Action of Stannous Chloride upon Nitrogen Iodide.

Stannous chloride, dissolved in the least possible quantity of dilute hydrochloric acid, readily reacts with nitrogen iodide, and if it be added slowly a little iodine is liberated. If the addition be continued till this liberated iodine just disappears, stannic chloride, ammonium chloride, and hydriodic acid alone are formed. The latter can be estimated by converting it into iodic acid by a solution of potassium permanganate, the ammonium being first expelled by a slight excess of caustic soda. The quantity of hydriodic acid formed is found to be half the amount equivalent to the stannous chloride oxidized.

Number of experiment.	$\frac{N}{I_2}$ SnCl_2 oxidized. cc.	$\frac{N}{I_2}$ HI produced. cc.	Ratio.
I	32.5	16.6	2 : 1.009
II	31.4	15.8	2 : 1.006
III	40.2	20.1	2 : 1
IV	30.7	15.5	2 : 1.009
VI	30.1	15.1	2 : 1.003
VII	27.9	14	2 : 1.003

The ratio usually comes out slightly too high. This, as in the case of sulphurous acid, is due to a small quantity of the nitrogen iodide breaking down into nitrogen and hydriodic acid under the influence of the hydrochloric acid which must be present to keep the stannous chloride in solution.

Action of Hydrogen Sulphide on Nitrogen Iodide.

On a solution of hydrogen sulphide being added to nitrogen iodide suspended in water the solid particles rapidly disappear, sulphur is precipitated, and ammonia and hydriodic acid are produced as in other cases. If the solution of hydrogen sulphide be very slowly added, iodine is set free, and the end of the reaction can be recognized easily by its disappearance. The investigation of this action is complicated by the circumstance that during it a considerable portion of the nitrogen iodide decomposes into nitrogen and hydriodic acid, and thus the ratio between the hydrogen sulphide oxidized and the hydriodic acid produced appears too great if the latter is directly estimated.

The following estimations show that the ratio thus obtained is variable but approximately 2 : 1.2.¹ The hydriodic acid was determined by adding a small excess of silver nitrate and estimating this excess by potassium thiocyanate.

Number of experiment.	$\frac{N}{10}$ $\frac{H_2S}{2}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	28.4	16.7	2 : 1.18
II	31.2	18.9	2 : 1.21
III	27.3	16.8	2 : 1.23
IV	33	19.8	2 : 1.2
VI	31.6	19.5	2 : 1.23
VII	35.8	22.5	2 : 1.26

As, however, the composition of nitrogen iodide has been definitely determined, the amount which actually reacts with the hydrogen sulphide and consequently the quantity of hydriodic acid liberated can be calculated from the ammonia formed. In the following experiments this was done, the nitrogen iodide which breaks up into nitrogen and hydriodic acid being neglected :

Number of experiment.	$\frac{N}{10}$ $\frac{H_2S}{2}$ oxidized. cc.	$\frac{N}{10}$ HI produced. cc.	Ratio.
I	30.8	15.4	2 : 1
II	24.7	12.3	2 : 0.995
III	32.2	16.2	2 : 1.006
IV	40.4	20.3	2 : 1.005
VI	26.8	13.4	2 : 1
VII	20.9	10.5	2 : 1.004

It is seen that the action of hydrogen sulphide upon nitrogen iodide is perfectly normal and that the amount of hydrogen sulphide oxidized is twice that equivalent to the hydriodic acid produced.

The close agreement between all the results obtained with such very different reducing agents places it beyond doubt that, when nitrogen iodide reacts with any reducing agent, the ratio between the amount of the latter oxidized and that of the hydriodic acid produced is as 2 : 1 ; in other words,

¹ Compare Bineau's (*Ann. chim. phys.* [3], 15, 71 (1845)) and Gladstone's (*Chem. Soc. J.*, 4, 34 (1852), and 7, 51 (1854)) analytical results obtained by this method. They differ among themselves, and this accompanying decomposition was not observed.

that the iodine contained in nitrogen iodide behaves in these reactions like the chlorine contained in a hypochlorite and exerts twice its normal oxidizing action.

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Contributions from the Chemical Laboratory of Harvard College.

CXVII.—ON CERTAIN COLORED SUBSTANCES DERIVED FROM NITRO COMPOUNDS.

[THIRD PAPER.¹]

BY C. LORING JACKSON AND F. H. GAZZOLO.

The colored substances formed by the action of sodic alcoholates and certain nitro compounds have been studied by Victor Meyer,² Lobry de Bruyn,³ and in this laboratory,⁴ but as yet no satisfactory constitutional formula has been assigned to them.

In continuing this investigation we tried first to replace the sodic alcoholates by other similar reagents, and succeeded in obtaining colored products from trinitranisol or trinitrobenzol by the action of sodic malonic ester, sodic acetacetic ester, sodic phenylate, the sodium compound of benzyl cyanide, and perhaps the sodium compound of phloroglucine, although in this last case the action was not well marked. As it has been shown already that similar compounds are formed with various sodic alcoholates,⁵ and even with sodic hydrate,⁶ it appears that this behavior with nitro compounds is a very general reaction of alkaline substances.

Of these new colored products only those with sodic malonic ester or sodic acetacetic ester were stable enough to be prepared for analysis, but they were unusually stable for bodies of this class. All four of the substances formed from trinitranisol or trinitrobenzol, and these two sodium esters were analyzed and were proved to consist of 3 molecules of the

¹ Presented to the American Academy of Arts and Sciences, December 13, 1899.

² Ber. d. chem. Ges., **27**, 3153; **29**, 848.

³ Rec. Trav. Chim. Pays-Bas., **14**, 89, 150; **15**, 848.

⁴ Jackson and Ittner: This JOURNAL, **19**, 199, where a historical account of the previous work is given; Jackson and Boos: *Ibid.*, **20**, 444.

⁵ *Ibid.*, **20**, 444.

⁶ Hepp: Ann. Chem. (Liebig), **215**, 359.

sodium ester combined with 1 of the trinitro compound; for instance, the malonic ester trinitrobenzol compound has this formula, $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]$. The formation of compounds with 3 molecules of the sodium constituent is noteworthy, since all the compounds analyzed heretofore have contained the two constituents in the proportion of 1 molecule of each. Similar experiments with sodic methylete, ethylete, or amylete and trinitrobenzol also led to products apparently containing 3 molecules of the alcoholate to each molecule of the nitro compound¹—a surprising result, since Lobry de Bruyn and Van Leent² obtained from trinitrobenzol a substance with the following formula, $C_6H_3(NO_2)_3KOCH_2\frac{1}{2}H_2O$. The difference in the result is unquestionably due to differences in the method of preparation. Lobry de Bruyn and Van Leent's compound was obtained by crystallization, whereas all our products with 3 molecules of the alkaline material were precipitated from an alcoholic solution with benzol. Experiments are now in progress to test this explanation of the phenomena.

The discovery of these sodic malonic or acetacetic compounds would furnish a strong argument, if that were needed, against the only theory of these colored substances as yet published—that of Victor Meyer,³ who supposed they were formed by the replacement of atoms of hydrogen on the benzol ring by atoms of sodium. This theory has been disproved by the observations of Lobry de Bruyn,⁴ supported by those made in this laboratory;⁵ and among other arguments the point was made that Victor Meyer's theory necessitated the assumption of alcohol of crystallization in every compound of this class which had been analyzed. In these malonic and acetacetic compounds the presence of malonic ester or acetacetic ester of crystallization must be assumed, if this theory is

¹ The ethyl and methyl compounds seemed to contain alcohol of crystallization, to judge from the percentages of sodium obtained. The publication of these results will, therefore, be postponed until further analytical data have been collected. The amyl compound, on the other hand, gave a percentage of sodium corresponding to $C_6H_3(NO_2)_3(NaOC_5H_{11})_3$.

² Rec. Trav. Chim. Pays-Bas., 14, 150.

³ Ber. d. chem. Ges., 27, 3153.

⁴ Rec. Trav. Chim. Pays-Bas., 14, 89.

⁵ This JOURNAL, 20, 445.

adopted; and, further, the number of molecules of "ester of crystallization" corresponds in each case to the number of atoms of sodium; the view, therefore, that the colored bodies are addition and not substitution compounds is confirmed by these observations.

Other experiments were tried to study the effect on the formation of the colors of increasing or diminishing the negative nature of the aromatic constituent. That there is some effect of this sort has been shown already, since certain substituted toluols give less stable colored derivatives than the corresponding benzoic acids.¹ Picramide, the first substance selected for this work, gave colored compounds with sodic methylate or sodic malonic ester, but too unstable to analyze, whereas trinitranisol or trinitrobenzol, in which the negative character of the nitro groups is not weakened by the presence of a positive radical like NH_2 , gave stable, well-marked colors. Dinitroxylol $((\text{CH}_3)_{1.3}(\text{NO}_2)_{4.6})$ also gave a slight and evanescent coloration with sodic methylate, and no reaction with sodic malonic ester, whereas trinitroxylol $((\text{CH}_3)_{1.3}(\text{NO}_2)_{2.4.6})$ gave colored compounds with both these reagents, which, although much more stable, could not be prepared for analysis. These results, therefore, as far as they go, show that an increase in the negative nature of the aromatic constituent increases the tendency to form colored compounds.

The next subject considered by us was the effect of the presence of methyl groups attached to the benzol ring on the formation of colors. Dinitrotoluol $((\text{NO}_2)_{2.4})$ gave colored compounds with sodic methylate or sodic malonic ester; dinitroxylol $((\text{CH}_3)_{1.3}(\text{NO}_2)_{4.6})$ gave only a passing coloration² with sodic methylate, none at all with sodic malonic ester; and dinitromesitylene gave no color with either reagent. Trinitroxylol gave strong color reactions with both reagents; trinitromesitylene none whatever. It is evident, therefore, that the presence of methyl groups on the benzol ring diminishes the tendency to form these colored compounds. Whether

¹ This JOURNAL 19, 201.

² This may have been due to a small quantity of a thiophene compound. As a rule we have not considered that a colored product belonged to the class we are studying unless we could obtain a copious precipitate of it with benzol.

this effect is due to a specific action¹ of the methyl group, or to the fact that these groups stand in the ortho position to the nitro groups, or to both these causes, cannot be determined from the facts at present at our disposal.

In consideration of the complete absence of a color reaction with trinitromesitylene and sodic methylate, it is interesting to note that M. Konowalow² obtained red salts from nitromesitylenes in which one of the nitro groups stands in the side chain. We cannot find that he analyzed these salts to determine whether they were true salts or addition-products with sodic hydrate. If the latter, they would have a strong bearing on the discussion given above.

Another series of experiments was tried with aromatic bodies rich in negative radicals by containing no nitro groups; for, if colors of the same class could be obtained from these, it would prove that the addition of the alkaline substance took place on the benzol ring and not on the nitro group. We were encouraged to undertake these experiments by the striking resemblance in properties³ between our colored products and the green bodies made by Astre⁴ from the action of sodic alcoholates on quinone. In the quinones, however, the formation of hemiacetals⁵ is possible, and it may be that the green bodies belonged to this class; we accordingly used for our new experiments substances in which the formation of hemiacetals could not occur, such as trimesic triethylester, which is especially fit for these experiments, since it has a still stronger resemblance to trinitrobenzol than quinone has, because it contains three negative radicals symmetrically disposed. We have not succeeded in obtaining any colored or other addition-products from this substance, or from the free trimesic acid, although the attempts have been repeated often and under varying conditions. Nor did we have better success with other bodies free from nitro groups, such as phloroglucine, or resorcine; pyrocatechine, it is true, gave a temporary coloration with sodic methylate, but we think this re-

¹ Lobry de Bruyn: *Rec. Trav. Chim. Pays-Bas.*, **14**, 95.

² *Ber. d. chem. Ges.*, **29**, 2304.

³ *This JOURNAL*, **20**, 446.

⁴ *Compt. rend.*, **121**, 530 (1895).

⁵ *This JOURNAL*, **17**, 579, 633.

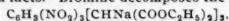
action does not belong to the series under discussion. These experiments, as they have given negative results, throw no light on the constitution of our colored compounds.

It has been shown earlier in this paper that the only theory as yet proposed for these colored compounds (that of Victor Meyer) is inadmissible, because they are addition-, not substitution-products. The facts now at our disposal are not sufficient to furnish an absolute proof of the structure of these compounds, but it is possible to show that certain constitutional formulas explain these facts better than others, and it seems to us that the work has arrived at a point where such a discussion of the possible formulas will be useful. In this discussion the following properties must be considered, as they seem to be characteristic of all the members of this group: (1) The very marked color. (2) The ease with which they are decomposed even by dilute acids, giving the aromatic constitution unaltered. (3) Their behavior with alcohols, which we describe here in some detail, because the principal observations are new. When the methyl compound, $C_6H_3(NO_2)_3OCH_3NaOCH_3$, is allowed to stand for some time with benzyl alcohol, both the methyls are replaced by benzyls, and the compound $C_6H_3(NO_2)_3OC_2H_5NaOC_2H_5$ is formed. Conversely this benzyl compound is converted into the corresponding methyl compound if boiled with methyl alcohol. In the same way the methyl is converted into the ethyl compound by crystallization from common alcohol.¹

There are three possible ways in which these compounds can be formed: *First*, The addition of the sodic methylete (or other alkaline substance) may take place upon the carbon atoms of the benzol ring. *Second*, It may take place on the nitro group alone. *Third*, It may take place partly on the nitro group and partly on the carbon of the benzol ring.

¹ This JOURNAL, 20, 449.

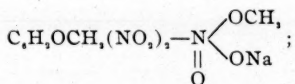
² Some experiments of less importance may be mentioned here, with the remark that they are not incompatible with the formula adopted later as giving the best explanation of the observed facts. Bromine decomposes the salt



giving trinitrobenzol as one of the products of the reaction. No salts with other basic radicals could be obtained from $C_6H_3(NO_2)_3OCH_3NaOCH_3$. No sodic iodide was formed by heating $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$ with ethyl iodide to 140°. On the other hand, it looked as if benzoyl chloride acted on these bodies, but the end of the college year prevented us from studying this reaction.

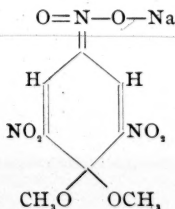
The first method of addition, that on the carbon alone, seems to us much less probable than the second or third, in which a nitro group takes part, especially since the work of Nef and others has shown that the sodium is attached to the nitro group in the sodium salt of nitromethane. As we have succeeded in finding no analogous case in which an alkaline substance is added to carbon atoms with the formation of a strongly colored product, we think that this first hypothesis is not worthy of a detailed discussion.

Turning to the formulas in which the nitro group is affected, we have the second method of addition, in which the sodic methylete is attached to the nitro group only; this would give rise to a structure such as the following:¹

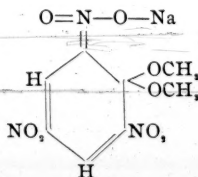


I.

while the third hypothesis, according to which both the nitro group and the carbon of the phenol ring take part in the addition, would be represented by the formulas given below, in which it is supposed that an isonitro² compound is formed with the development of a quinoid structure in the benzol ring. The difference between the two formulas is that in II the quinoid structure is developed in the para position, in III in the ortho position:



II.



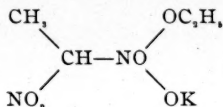
III.

¹ This is analogous to that given by Hantzsch and Rinckenberger (Ber. d. chem. Ges., **32**, 628) for their dinitroethanester acid.

² Compare Hantzsch (Ber. d. chem. Ges., **32**, 575-651) and also the orthobenzoldioxime of Zincke and Schwarz (Ann. Chem. (Liebig), **307**, 28).

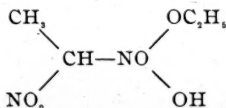
We have used the formula of the addition-product from sodic methylate and trinitranisol, as it is the simplest that will serve in the argument which follows. In applying these formulas to the malonic ester compounds it must be assumed that the malonic ester radical which is added to the benzol ring has the constitution $-\text{OC}(\text{OC}_2\text{H}_5)=\text{CHCOOC}_2\text{H}_5$, as, if it is assumed to be $-\text{CH}(\text{COOC}_2\text{H}_5)_2$, we should have an attachment of carbon to carbon incompatible with the instability of these compounds.

In applying formulas I, II, and III to the explanation of the observed properties of these compounds, we consider first the strong color, their most marked characteristic; this is explained by the quinoid structure in formulas II or III, but is not accounted for by formula I, since, according to Hantzsch and Rinckenberger,¹ their substance

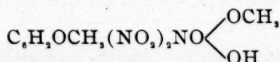


which contains the group characteristic of formula I, has only a pale-yellow color.

The easy decomposition of the colored body by hydrochloric acid with regeneration of the trinitranisol, from which it was formed, is accounted for by either of the three formulas, I, II, or III, but the preference should be given to II or III, since Hantzsch and Rinckberger² state that their compound



is a true stable acid ten times as strong as acetic acid, and it is fair to suppose, therefore, that the substance

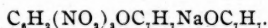


¹ Ber. d. chem. Ges., 32, 628.

² *Ibid.*

(formed by hydrochloric acid on our sodium salt, if it has formula I) would also be comparatively stable, and not drop at once into the trinitranisol, which, as a matter of fact, is formed immediately by the action of hydrochloric acid on the colored compound. On the other hand, this rapid decomposition by acid would be explained according to formula II or III by the strong tendency of quinoid bodies to pass into the hydroquinoid form, which might easily cause the splitting off of methyl alcohol as soon as the atom of sodium was replaced by hydrogen. This rapid decomposition with removal of methyl alcohol when the colored bodies are treated with dilute hydrochloric acid recalls the similar behavior of the dichlorodimethoxyquinonedimethylhemiacetal;¹ and the similarity of these phenomena may tell in favor of classing the colored salts with quinone derivatives, although the two reactions are not strictly analogous.

The third point in favor of formula II or III is the replacement of the two methyls in $C_6H_2(NO_2)_2OCH_3NaOCH_3$ by benzyls when the compound is soaked in benzyl alcohol, and the reverse change when the benzyl compound is boiled with methyl alcohol. As under the same conditions benzyl alcohol has no action on methyl picrate, or methyl alcohol on benzyl picrate, it is obvious that the complete replacement of one radical by the other here depends on the structure of the addition-product; and, whereas formula I gives no reason why the change should proceed beyond the methyl attached to the nitro group, it is easy to see that in a substance constituted like formula II or III any reagent which affected one methyl would act in a similar way on the other, so that the methyl compound would be completely converted into



The inferences drawn in the foregoing discussion may be briefly recapitulated as follows: It is improbable that the sodic methylate is added to the carbon of the benzol ring only. A quinoid formula (II or III) explains the observed facts better than one in which the sodic methylate is added to the nitro group alone (I), but this latter structure is not definitely ex-

¹ This JOURNAL, 17, 604.

cluded. Under these circumstances we think it would be premature to contrive names for these colored bodies, or to give structural formulas in the experimental part of this paper. We hope that a continuation of the work, now in progress in this laboratory, will definitely settle the constitution of these colored substances.

EXPERIMENTAL PART.

Preparation of Picryl Chloride.

As the method of making picryl chloride used by us in this work is an improvement on that given by Pisani,¹ we describe it. Twenty-five grams of dry picric acid were mixed with 50 grams of phosphoric pentachloride in a large Erlenmeyer flask provided with an air condenser, and heated on the water-bath until the violent reaction had ceased, and the contents had assumed a very dark-brown color. When cold, the flask was surrounded with ice, and its contents treated with ice-water, care being taken to avoid any considerable rise of temperature. The precipitate formed in this way was filtered out, dried, washed with ether, and crystallized from a mixture of benzol and alcohol to purify it. The advantages in our method are that there is a considerable saving of time, and there is much less danger that the substance will be converted into a tarry decomposition-product, as happens in Pisani's method if the heat runs too high in either the preparation or the removal of the phosphoric oxychloride by distillation.

Action of Sodac Acetacetic Ester with Trinitranisol.

In our first experiment in this direction we prepared our sodac acetacetic ester with sodic methylete, and obtained a red precipitate which gave the following result on analysis:

0.2438 gram substance gave 0.0576 gram Na_2SO_4 .

Na	Calculated for	Found.
	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_2\text{NaOCH}_3$	
	7.69	7.66

It was evident, therefore, that we had only the color formed from sodic methylete, and that the acetacetic ester took no part in the reaction. In order, then, to obtain an acetacetic ester

¹ Ann. Chem. (Liebig), 92, 326.

addition, it was obviously necessary to exclude all alcohol and alcoholates; we accordingly proceeded as follows: To an excess of acetacetic ester mixed with benzol a quantity of sodium in the form of ribbon was added (in our later preparation the amount of sodium used provided 3 atoms of it to each molecule of trinitranisol). After the sodium had disappeared, the liquid thus obtained was added drop by drop to a benzol solution of trinitranisol. It is unnecessary to say that absolute benzol was used in all this work. The first drop imparted a deep vermilion color to the solution, and this color became more and more intense as the reaction proceeded. During the process the mixture was kept cool by surrounding the beaker with ice. After all the sodic acetacetic ester had been added, the liquid was mixed with an excess of anhydrous benzol, which threw down a semi-gelatinous or oily precipitate. This was filtered out, washed with benzol, and pressed upon a porous plate, all these operations being carried on as quickly as possible. The dark-colored dried product crumbled easily into a red amorphous powder of a much darker color than the addition-product from sodic methyllate. It was dried *in vacuo* and analyzed with the following results:

I. 0.2376 gram substance gave 0.0740 gram Na_2SO_4 .

II. 0.2196 gram substance gave 0.0697 gram Na_2SO_4 .

III. 0.1928 gram substance gave 0.0700 gram Na_2SO_4 .

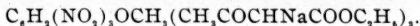
IV. 0.2596 gram substance gave on combustion 0.4028 gram CO_2 and 0.1148 gram H_2O . In this combustion the substance was mixed with chromic oxide to drive out carbonic dioxide from the carbonate formed, and was spread out in a long copper boat, which was heated gently and gradually to avoid explosions.

	Calculated for	Found.			
	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_2(\text{CH}_2\text{COCHNaCOOC}_2\text{H}_5)_3$	I.	II.	III.	IV.
Na	9.87	10.10	10.28	11.75	
C	42.91				42.32
H	4.57				4.91

There can be no doubt, therefore, as each analysis is of the product of a separate preparation, that the substance is a definite compound, and is formed by the addition of 3 molecules of sodic acetacetic ester to 1 of trinitranisol. The varia-

tion in the percentages of sodium in the different specimens is no more than would be expected, when it is remembered that the product was purified only by washing with benzol.

Properties of the Addition-product of Trinitranisol and Sodac Acetacetic Ester,



This substance forms a deep crimson powder, which we have not succeeded in bringing into a crystalline state. It is decidedly stable for a body of this class, keeping for several days in a desiccator, but finally decomposing into a black tar. When heated it is slightly explosive. It dissolves completely in water without decomposition, to judge from the color; is soluble in common alcohol, but gives a turbid solution; on the other hand, it dissolves, forming a clear solution, in methyl alcohol; soluble in acetone; insoluble in benzol, ether, chloroform, carbonic disulphide, or ligroin. Acids decompose it instantly, as was shown by the destruction of the color.

Action of Sodac Malonic Ester on Trinitranisol.

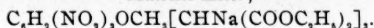
Two grams of trinitranisol dissolved in absolute benzol were mixed with a benzol solution of 4.5 grams of sodac malonic ester prepared by the direct action of sodium on the malonic ester,—that is, 3 molecules of the sodium ester to each molecule of trinitranisol. As the two solutions came together, an intense cherry-red color appeared, with the formation of a thick gelatinous precipitate of the same color, which increased in volume and deepened in color as the reaction continued. After the mixture had stood some time at ordinary temperatures, a large enough quantity of benzol was added to produce complete precipitation, the product was then filtered rapidly, washed with benzol till the filtrate was colorless, pressed quickly on the porous plate, and dried *in vacuo*. This reaction seemed to run more quickly and clearly than the corresponding one with sodac acetacetic ester, giving a purer product, which was very easily handled and washed.

I. 0.0208 gram substance gave 0.0536 gram Na_2SO_4 .

II. 0.3027 gram substance gave 0.0796 gram Na_2SO_4 .

Calculated for		Found.	
$C_6H_2(NO_2)_3OCH_2[CHNa(COOC_2H_5)_2]_x$		I.	II.
Na	8.74	8.56	8.52

Properties of the Addition-product of Trinitroanisole and Sodium Malonic Ester,



This substance is an amorphous powder with a deep maroon color. We have not succeeded in crystallizing it. It is one of the most stable bodies of its class, as when exposed to the air it usually remains unaltered for nearly five days; at the end of this time it begins to grow moist, then turns black, and is finally converted into a black powder with a somewhat tarry consistency. When heated it explodes with a slight puff, but with little or no noise; it is, however, apparently stable at as high a temperature as 140° . It dissolves completely in water, forming a clear cherry-red solution; soluble, although more slowly, in ethyl alcohol; completely and quickly soluble in methyl alcohol, but this solution seems to be attended by some decomposition, as a fading of the color was observed; soluble in acetone; insoluble in ether, benzol, chloroform, carbonic disulphide, or ligroin. A few drops of hydrochloric acid added to its aqueous solution changes the red color to yellow instantly, and causes a precipitate which, on filtration, solution in alcohol, and evaporation of the solvent, proves to be a reddish oil containing malonic ester, to judge from the smell, and trinitroanisole, since this substance crystallizes out on standing.

As this substance was more stable than most others of its class, we tried the action of ethyl iodide upon it in the hope of replacing the atoms of sodium with ethyl. For this purpose 0.5 gram of the addition-product was heated in a sealed tube with ethyl iodide, at first to 100° , but, as this produced no apparent effect, later to 140° for an hour and a half, and then it was kept at 100° for two days. The contents of the tube were treated with benzol, after the ethyl iodide had evaporated, which gave a red solution and a black residue; the residue was extracted with water, and the extract gave no test for an iodide. It is obvious, therefore, that the ethyl iodide had not acted at all, but that the unmanageable black

product was produced by the decomposition of the addition compound.

Action of Sodid Malonic Ester with Trinitrobenzol.

The sodic malonic ester was prepared with sodium alone, benzol was used as the solvent, and the proportions were 3 molecules of the ester to 1 of the trinitrobenzol. As soon as the solutions were mixed, a deep-scarlet, lumpy precipitate was formed; it was found best, therefore, to add the solution of the sodic malonic ester in small portions at a time with constant stirring. The beaker was cooled by immersing it in ice. The precipitate was washed with benzol until the filtrate was colorless, and then dried on a porous plate and *in vacuo*. Analyses I and II are of 2 different products prepared in this way. As in these preparations and the other similar one described in this paper we had used 3 molecules of the sodium compound to one of the nitro body, there seemed some danger that our products might not be definite compounds, but mixtures of an addition compound containing only 1 atom of sodium, with the two additional molecules of the sodic malonic ester (or the corresponding reagent) precipitated by the large excess of the benzol. This objection to our results did not seem a very important one, because they agreed better with the theoretical numbers than would be probable if this theory were true, but we felt that it was necessary to test it by experiment, and for this purpose repeated the preparation, using 2 molecules of sodic malonic ester to each molecule of trinitrobenzol (1 gram of trinitrobenzol and 1.7 grams of the sodic malonic ester). Analysis III was made with the specimen prepared in this way, and proves that our substances are definite compounds and not mixtures, since it agrees with those prepared with 3 molecules of the sodium ester.

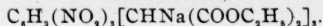
I. 0.2038 gram substance gave 0.0544 gram Na_2SO_4 .

II. 0.2154 gram substance gave 0.0590 gram Na_2SO_4 .

III. 0.2630 gram substance gave 0.0756 gram Na_2SO_4 .

Na	Calculated for	Found.		
	$\text{C}_6\text{H}_2(\text{NO}_2)_3[\text{CHNa}(\text{COOC}_2\text{H}_5)_2]_3$	I.	II.	III.
	9.09	8.66	8.87	9.31

Properties of the Addition-product of Trinitrobenzol and Sodid Malonic Ester,



This body has a rich maroon color brighter than that of the corresponding compound of trinitranisol and sodic malonic ester. It is stable for some time if kept dry and cool, otherwise it gradually undergoes decomposition, as shown by its change of color and becoming gummy. In its other properties it resembles the corresponding trinitranisol compound most closely. When treated with hydrochloric acid the color is destroyed, and a thick brownish-yellow precipitate is formed; by washing this with small quantities of alcohol to remove the malonic ester the trinitrobenzol was recovered in quantity, and recognized by its melting-point, 121° – 122° , after crystallization from benzol. As soon, therefore, as the three atoms of sodium are replaced by hydrogen the addition-product splits into its constituents.

Action of Bromine on the Addition-product of Trinitrobenzol and Sodid Malonic Ester.

The addition-product, $\text{C}_6\text{H}_3(\text{NO}_2)_3[\text{CHNa}(\text{COOC}_2\text{H}_5)_2]$, was added in small successive portions to a chloroform solution of bromine cooled by immersing the vessel in ice. The color of the solid changed instantly from maroon to white. After the mixture had stood over night, the solid was filtered out and the filtrate allowed to evaporate spontaneously, when it left a thick brownish-red oil, which, after standing two days, deposited crystals identified as trinitrobenzol by their melting-point, 221° , the form of the crystals, and the formation of the characteristic red color with sodic alcoholates. The portion insoluble in chloroform, after thorough washing with chloroform and boiling benzol, proved to be sodic bromide. This experiment does not absolutely disprove the formation of some bromtrinitrobenzol, since a small amount of it might have remained dissolved in the oil from which the trinitrobenzol was deposited, but it shows that trinitrobenzol is one of the principal products of the reaction; and as this separated from the oil in a nearly pure state, it is very probable at least that no bromtrinitrobenzol was formed.

Action of Acetacetic Ester on Trinitrobenzol.

The product was prepared in the same way as the corresponding addition compound of trinitrobenzol and sodic malonic ester. In this case the precipitate had a deeper red color than that produced with sodic malonic ester, and the reaction ran less neatly. Analyses of three different preparations dried *in vacuo* gave the following results:

- I. 0.1865 gram substance gave 0.0623 gram Na_2SO_4 .
- II. 0.2017 gram substance gave 0.0658 gram Na_2SO_4 .
- III. 0.2104 gram substance gave 0.0680 gram Na_2SO_4 .

Na	Calculated for	Found.		
	$\text{C}_6\text{H}_3(\text{NO}_2)_3[\text{CH}_2\text{COCHNaCOOC}_2\text{H}_5]_3$	I.	II.	III.
	10.32	10.82	10.56	10.47

The addition-product of trinitrobenzol and sodic acetacetic ester is a rich brownish-red amorphous powder darker than the corresponding product from trinitrobenzol and sodic malonic ester. It is fairly stable if kept dry. In its other properties it is exactly similar to the colored substances already described in this paper.

Preparation of the Trisodic Amylate Addition-product of Trinitrobenzol.

To a benzol solution of 1 gram of trinitrobenzol 1.5 grams of sodic amyrate were added gradually, care being taken to keep the mixture cool. The proportions are 3 molecules of the amyrate to each molecule of trinitrobenzol. A heavy scarlet precipitate was formed as soon as the substances came together; this was filtered quickly, thoroughly washed with benzol, and dried on a porous plate, after which it was analyzed, with the following results:

- I. 0.2596 gram substance gave 0.1070 gram Na_2SO_4 .
- II. 0.1700 gram substance gave 0.0680 gram Na_2SO_4 .
- III. 0.3190 gram substance gave 0.1288 gram Na_2SO_4 .

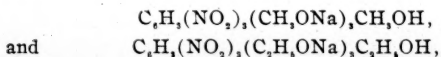
Na	Calculated for	Found.		
	$\text{C}_6\text{H}_3(\text{NO}_2)_3(\text{C}_2\text{H}_{11}\text{ONa})_3$	I.	II.	III.
	12.71	13.36	12.96	13.07

Properties of Trisodic Amylate Addition Compound of Trinitrobenzol, $\text{C}_6\text{H}_3(\text{NO}_2)_3(\text{C}_2\text{H}_{11}\text{ONa})_3$.

The dry substance is a dark-crimson amorphous powder.

It is remarkably stable for bodies of this class, since it did not change in color, or show any tendency to become moist, even after standing for two weeks in contact with the air. It is soluble in ethyl or methyl alcohol or acetone; very soluble in water; insoluble in benzol, chloroform, carbonic disulphide, or ligroin. The strong acids decompose it at once, giving trinitrobenzol as one of the decomposition-products.

Upon treating trinitrobenzol with sodic methyrate or sodic ethylate under the same conditions, products were obtained with the following formulas, if we may judge from the sodium determinations:



but as these seem an insufficient foundation for such formulas, we shall postpone the description of these substances until we have collected sufficient analytical data to establish their composition. They are both red, but decompose more rapidly than the amylate, becoming moist and discolored after exposure to the air for a few hours. Heating also decomposes the methyrate body, so that the presence of methyl alcohol of crystallization could not be established in this way. The discussion of the conditions under which these tri bodies are formed instead of the mono compounds will also be postponed until it has been thoroughly settled by further experiments.

Attempts to obtain Colored Compounds with other Reagents.

Sodic phenylate, made by adding sodium to an excess of phenol, gave with trinitrobenzol a clear red color, but no precipitate. A similar result was obtained when an alcoholic solution of sodic phenylate was added to a benzol solution of trinitroanisol; but this latter coloration does not necessarily proceed from the sodic phenylate, as part of it may have been converted into sodic ethylate by the alcohol.

Sodic hydrate also gives a red color with trinitrobenzol, as was observed by Hepp,¹ but as there seemed little chance of isolating this in a state fit for analysis, we did not attempt to study it.

¹ Ann. Chem. (Liebig), 215, 359.

The sodium salt of phloroglucine, made by treating an excess of it with sodic hydrate, gave a light-reddish color when treated with a benzol solution of trinitrobenzol, and upon adding an excess of benzol a most uninviting sticky precipitate was formed which it would have been foolish to try to analyze. We doubt whether this colored substance was really a phloroglucine compound, as it is very possible that it was formed from a little sodic hydrate produced by the decomposition of the sodium salt of the phloroglucine.

Benzyl cyanide, treated with metallic sodium, after the slight action with the sodium was finished, was mixed with trinitrobenzol. Upon stirring for a few seconds a deep blood-red precipitate appeared in large quantity; but it was so unstable that even the addition of benzol to wash out the excess of benzyl cyanide converted it into a black, tarry mass, so that we were obliged to give up all idea of analyzing it.

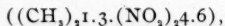
Attempts to obtain Colored Compounds from other Nitro Bodies.

Picramide, $C_6H_3(NO_2)_3NH_2$, treated with a mixture of sodic methylate, methyl alcohol, and anhydrous benzol, gave at once a strongly colored, dark-crimson solution, which deposited a brick-red precipitate; but in collecting it for analysis the substance decomposed as soon as it dried on the porous plate, forming a brownish mass, which later became tarry. We were unable, therefore, to make an analysis.

Trichlorbromdinitrobenzol ($Cl_3,1.3.5.Br_2(NO_2)_4.6$) gives a strong vermilion color with an alcoholic solution of sodic ethylate, as already stated by us in a previous paper.¹

Dinitrotoluol ($(NO_2)_2.2.4$) melting at $70^\circ.5$, gave with sodic methylate a deep vermilion-colored solution, from which a precipitate was obtained with an excess of benzol. A benzol solution of the dinitrotoluol gave with sodic malonic ester a crimson-red solution and a colored precipitate, but both this and the precipitate of the methylate compound decomposed while drying on the porous plate.

Symmetrical dinitroxytol, melting at 93° ,



gave with sodic methylate, after a few seconds, a faint green-

¹ This JOURNAL, 22, 58.

ish color, which turned rapidly to a deep purple, and finally became brownish-black. It was evidently, therefore, very unstable. Neither sodic malonic ester nor sodic acetacetic ester gave any trace of color.

Trinitroxylol ($(\text{CH}_3)_{1.3}(\text{NO}_2)_{2.4.6}$) gave a deep cherry-red solution with either sodic methylate or a benzol solution of sodic malonic ester or of sodic acetacetic ester. An excess of benzol precipitated from each of these solutions a gummy, reddish body, which decomposed before it could be prepared for analysis. In these cases the decomposition-product had a pinkish-white color.

Neither dinitromesitylene nor trinitromesitylene gave a trace of color after standing with sodic methylate. At the moment the trinitromesitylene was mixed with the sodic methylate we thought in one or two cases we perceived a very faint coloration, but it was so indistinct that we felt doubtful of its existence, and at best it was very evanescent. Sodic malonic ester and sodic acetacetic ester also gave negative results with both these bodies.

Dinitrophenylglucinetriethyl ether, $\text{C}_6\text{H}(\text{OC}_2\text{H}_5)_2(\text{NO}_2)_2$, gave no color with sodic methylate, sodic malonic ester, or sodic acetacetic ester.

Attempts to Obtain Colored Compounds from Bodies which Contain no Nitro Group.

Pyrocatechin gave no color with sodic malonic ester, but with sodic methylate a bright-green color was formed along the edges, which soon darkened, and finally gave a black oil. This coloration is probably similar to those observed by Kunz Krause¹ on treating various phenols with sodium and alcohol, but we do not feel sure that these colors are related to those obtained from nitro compounds.

Resorcline gave no color with either sodic methylate, sodic malonic ester, or sodic acetacetic ester. The same negative results were obtained with phloroglucine.

Neither trimesic acid, $((\text{COOH})_{1.3.5})$, nor its ester, $\text{C}_6\text{H}_2(\text{COOC}_2\text{H}_5)_3$, gave any sign of sodic methylate, although the experiments were tried with great care, and under condi-

¹ Arch. Pharm., 236, 542.

tions which gave colors even with some of the less reactive nitro compounds.

Experiments on the Replacement of the Allyl Radical in the Colored Compounds.

Action of Methyl Alcohol on the Benzyl Compound.—The addition product of benzyl picrate and sodic benzylate, discovered by W. F. Boos and one of us,¹ was heated with methyl alcohol for about half an hour, and the methyl alcohol was then allowed to evaporate at ordinary temperatures. The product consisted of glistening scarlet crystals, which were at once decolorized by hydrochloric acid, yielding a substance melting at 64°, and crystallizing in yellow rhombic plates from benzol. It was therefore trinitranisol, and the methyl alcohol had replaced the benzyl groups in the original addition-compound by two methyls.

Action of Methyl Alcohol on Benzyl Picrate.—Benzyl picrate was prepared according to the method given by Boos and one of us.² The melting-point of this substance is 145°, not 115° as given in the paper just cited; the number 115° was due to a mistake in copying the melting-point from the note-book. A quantity of the benzyl picrate was recrystallized four times from boiling methyl alcohol, and after each crystallization the melting-point remained constant at 145°, thus showing that the benzyl picrate is not converted into methyl picrate by methyl alcohol at its boiling-point.

Action of Benzyl Alcohol on the Addition-product of Trinitranisol and Sodid Methylate.—The colored compound was dissolved in benzyl alcohol with the aid of gentle heat, and the mixture was allowed to stand at ordinary temperatures until crystals separated. The red substance obtained in this way was decomposed with hydrochloric acid, when the product, after crystallization, showed the constant melting-point 145°, and was therefore benzyl picrate. In this case, therefore, the benzyl alcohol had converted the colored methyl compound into the corresponding benzyl compound.

Action of Benzyl Alcohol on Trinitranisol.—A solution of

¹ This JOURNAL, 20, 452.

² *Ibid.*, 453.

trinitranisol in benzyl alcohol was allowed to stand in a paraffin desiccator until all the benzyl alcohol had evaporated; the residue showed the melting-point of trinitranisol, 64° .

Benzyl alcohol, therefore, does not affect trinitranisol under the conditions used in the experiment described in the last paragraph.

Attempts to Prepare Derivatives from the Addition Compound of Trinitranisol and Sodid Methylate.

Salts.—The sodium salt, $C_6H_2(NO_2)_3OCH_2NaOCH_3$, was treated with the salts of various metals in the hope of obtaining other salts. The chlorides of calcium, barium, mercury, and zinc, in mixed methyl alcohol and aqueous solutions, produced no change. Cupric chloride, on the other hand, formed a brown precipitate, from which trinitranisol was isolated, and tests were obtained for copper and picric acid. We decided, therefore, that the cupric chloride had decomposed the colored compound, and neither this nor any of the other experiments we tried seemed to point to the formation of salts of the colored compounds by metathetical reactions.

Treatment with Benzoyl Chloride.—The addition compound $C_6H_2(NO_2)_3OCH_2NaOCH_3$, if dissolved in methyl alcohol and treated with benzoyl chloride, was at once decolorized, even when sodid methylate was also present. Upon treating the dry compound with benzoyl chloride, and allowing the mixture to stand over night, the amorphous powder had become converted into masses resembling cauliflower, with an even more intense scarlet color than at first. An attempt to introduce the benzoyl group by the Baumann-Schotten method led to a similar result. One gram of the addition-product was added to 25 grams of an 18 per cent solution of sodid hydrate, and then 5 grams of benzoyl chloride were gradually poured into the mixture; the granular red powder was gradually converted into masses resembling cauliflowers, most of which dissolved in the alkaline liquid with a distinct intensification of the red color. On acidifying with hydrochloric acid, the color was discharged and a white precipitate of benzoic acid was formed. The filtrate apparently contained picric acid. Unfortunately we had not time to study this reaction more

carefully, but we hope it will be investigated in this laboratory during the coming year, and also that the behavior of this compound with methyl iodide may be studied then.

Postscript.—The manuscript of the foregoing paper was ready for the press, when I received an article¹ on colored compounds of this class by Hantzsch and Kissel, in which they ascribe to them formulas with the sodic alcoholate added to the nitro group only (I). I cannot find any reason in their article for changing the conclusion to which I had already come, that a quinoid formula (II or III) explains all the observed facts better than the formula (I) adopted by them. Their most important new facts are the isolation of the free acid from the addition-product of potassic methylate and trinitrotoluol, and the formation of the corresponding acetyl compound, both of which are explained better by the quinoid formula than by theirs. They also call attention to the fact that the free acid is a weak one instead of being a strong one, as it should be, if derived from a salt with their formula, and that the marked color of the compounds would not be expected from this structure; both of these anomalies disappear if the quinoid formula is adopted. It seems, therefore, that their observations tend to confirm this quinoid formula.

The authors also claim to have disproved definitely the theory of Victor Meyer that these bodies are substitution-products, but neglect to mention that Lobry de Bruyn,² in 1895, proved the incorrectness of this theory by treating trinitrobenzol in boiling xylol with sodium. Therefore all subsequent arguments against Victor Meyer's theory (of which I have furnished three) must be considered as only confirmatory of Lobry de Bruyn's work.

It may not be out of place to repeat here that work on this subject is still in active progress in this laboratory.

C. LORING JACKSON.

DECEMBER 27, 1899.

¹ Ber. d. chem. Ges., **32**, 3137 (1899).

² Rec. Trav. Chim. Pays-Bas., **14**, 89.

THE SOLUTION-TENSION OF ZINC IN ETHYL ALCOHOL.

BY HARRY C. JONES AND ARTHUR W. SMITH.

The conception of solution-tension of metals was first made use of by Nernst¹ to explain the action of primary cells. The chief seat of the electromotive force of such cells was shown to be at the surfaces of contact of the electrodes with the electrolytes. The magnitude of the potential which is produced when a bar of metal is immersed in a solution of one of its salts, is a function of two quantities: The osmotic pressure of the cations of the dissolved salt, and the solution-tension of the metal in question. These two forces act in opposition to each other; the osmotic pressure of the cations tending to drive these ions out of solution on to the metal, while the solution-tension of the metal tends to drive the metallic atoms off from the bar as ions, which would then remain in the solution.

The result of the reaction of these two opposing forces is to produce around the bar of metal the well-known Helmholtz² double layer. The metal atoms passing off into the solution as ions, take positive electricity from the bar of metal which thus becomes negative; the solution into which these cations pass, since it now contains an excess of cations, becomes positive.

The osmotic pressure of the cations, on the other hand, drives cations out of the solution on to the metal, the metal becoming positive due to the charge which it has received from these cations when they passed over into metallic atoms; the solution, having lost some of its cations, becomes negatively charged.

The action which will result in any given case depends upon the relative values of the solution-tension of the metal and the osmotic pressure of the cations of the salt.

There are three conditions possible. If we represent the solution-tension of the metal by P , and the osmotic pressure of the cations of the salt by p , we may have: (1) $P > p$; (2)

¹ Ztschr. phys. Chem., 4, 129.

² Ann. der Phys. (Wied.), 7, 337.

$P = p$; (3) $P < p$. In the first case, where the solution-tension of the metal is greater than the osmotic pressure of the cations, a small part of the metal will pass over into ions, or as we generally say, will dissolve. These ions carry positive electricity from the metal into the solution—the former becoming negative, the latter positive. The negative electricity on the metal would attract, electrostatically, the positive ions in the solution, and a double layer would be formed which would tend to drive the metallic ions out of the solution on to the metal. The attraction between the two parts of this double layer, which tends to drive the metallic ions out of the solution, acts against the solution-tension of the metal, and equilibrium will be established when these two opposing forces are equal.

If $P < p$, the above condition will be exactly reversed. Cations will separate from the solution upon the metal, which thus becomes positive with respect to the solution. The positive charge on the metal attracts, electrostatically, the negative ions in the liquid, and an electrical double layer is formed, but the reverse of the above. Metallic ions will separate from the solution until the electrostatic repulsion of these ions by the positive metal is equal to the osmotic pressure tending to force them out of solution.

In the second case, where $P = p$, nothing will happen. The formula which has been deduced¹ for calculating the potential between a metal and a solution of one of its salts is:

$$\pi = \frac{0.058}{v} \log \frac{P}{p},$$

in which π is the potential, v the valence of the metal, P the solution-tension of the metal, and p the osmotic pressure of the cations in the solution.

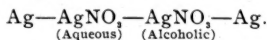
It is obvious that this equation can be used to calculate the solution-tension of the metal. It is only necessary to solve for $\log P$, and determine π and p .

It was supposed for a time that the solution-tension of a metal is a constant, independent of the nature of the solvent

¹ Nernst: *Ztschr. phys. Chem.*, 4, 129; Ostwald: *Lehr. d. allg. Chem.*, II, p. 851; Le Blanc: *Lehrb. d. Elektrochemie*, p. 123; Jones: *Theory of Electrolytic Dissociation*, p. 236.

in which it is immersed. Ostwald states¹ that "The solution-tension of a metal is a constant peculiar to the metal, which depends only on the temperature and generally increases with rise in temperature."

On the assumption that the solution-tension of a metal is a constant, Jones² studied the following cell:



The electromotive force of such an element can be calculated from the following equation:

$$\pi = 0.058 \left(\log \frac{p_1}{P_1} - \log \frac{p_2}{P_2} \right),$$

where p_1 is the osmotic pressure of the silver ions in the aqueous solution, P_1 the solution-tension of the silver in this solution, p_2 the osmotic pressure of the silver ions in the alcoholic solution, and P_2 the solution-tension of the silver in this solution. But since the solution-tension of a metal is a constant, $P_1 = P_2$, everything in the above equation is already known or could be measured, except p_1 , the osmotic pressure in the alcoholic solution. It seemed very probable to Jones that he had a general method for measuring dissociation in solvents other than water. It was only necessary to construct a cell using an aqueous solution of a salt of the electrode on one side, and a solution in some other solvent upon the other, in order to measure the dissociation of the salt in the other solvent. But these hopes were soon abandoned.

If the solution-tension of silver is the same in the alcoholic as in the aqueous solution, then the electrode immersed in the aqueous solution must be positive against the electrode in the alcoholic solution, since it was well known that p_2 is greater than p_1 . The first point discovered by Jones was that the alcoholic solution was positive against the aqueous. From this it was at once evident that the solution-tension of silver in the alcoholic solution was much less than in the aqueous solution. He then determined the value of the solution-tension.

¹ *Lehr. der. allg. Chem.*, II, 852.

² *Ztschr. phys. Chem.*, 14, 346.

sion in alcohol as compared with the solution-tension in water. The above equation,

$$\pi = 0.058 \left(\log \frac{P_1}{P_2} - \log \frac{P_3}{P_4} \right),$$

when solved for P_1 becomes :

$$\log P_1 = -\frac{\pi}{0.058} + \log \frac{P_3}{P_4} + \log P_2,$$

if $P_2 = 1$, $\log P_2 = 0$.

Jones measured the electromotive force of a number of cells containing an aqueous solution of silver nitrate on the one side and an alcoholic solution on the other. He calculated the solution-tension of silver in alcohol, using the approximate values for the dissociation of silver nitrate in alcohol which had been furnished by Völlermer.¹ He found that the solution-tension of silver in the alcoholic solution of its salt is about *one-twentieth* of that in the aqueous solution.

Jones has recently attempted to measure more accurately the dissociation of silver nitrate in ethyl alcohol, by means of the improved boiling-point method,² which has proved so efficient in other cases. He has, however, not been successful, since silver nitrate in boiling ethyl alcohol always undergoes more or less reduction.

The problem of the solution-tension of metals rested here until quite recently.

Kahlenberg³ has very greatly extended the work which was begun by Jones. He has used a number of metals as electrodes, and a number of solvents in which the salts of these metals were dissolved, and has entirely substantiated the conclusion reached by Jones, that the solution-tension of a metal is not a constant but varies for every solvent used.

He has not been able to calculate the absolute value of the solution-tension of many of the metals in the different solvents, because he had no means of measuring the dissociation of the salts of these metals in the several solvents. He has calculated the approximate solution-tension of silver in aceto-

¹ Ann. der. Phys. (Wied.), 52, 328.

² This JOURNAL, 19, 581; Ztschr. phys. Chem., 31, 114.

³ J. Phys. Chem., 3, 379.

nitrile, and finds that it is greater than in water. Similar results were obtained with silver in pyridine.

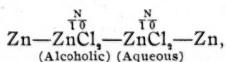
Kahlenberg¹ adds that "further attempts to calculate solution-tensions will not be made, seeing that the requisite values of p are not available;" p being the dissociation of the salts in the non-aqueous solutions.

It will be seen from the above that all that has been done, even up to the present, is to determine the relative solution-tensions of one metal—silver—in a very few solvents. Now it so happens that silver stands at one of the extremes of the tension series. It is the metal with the very smallest solution-tension. This will be seen from the following table of metals arranged in the order of their solution-tensions in aqueous solutions of their salts.

	Atmos.		Atmos.
Magnesium	10^{44}	Lead	10^{-2}
Zinc	10^{18}	Copper	10^{-9}
Aluminum	10^{13}	Mercury	10^{-15}
Cadmium	10^7	Silver.	10^{-15}
Iron	10^3		

The relations which obtain for silver with its infinitesimal solution-tension, might not exist for metals with a high solution-tension, and especially for metals with such enormous solution-tensions as those which stand near the head of the first column. It is, therefore, very desirable to determine the solution-tension of some metal high in the tension series, in different solvents, and see what variations obtain.

We have succeeded in doing this in the case of zinc immersed in an alcoholic solution of zinc chloride. The electromotive force of the element,



was measured by Kahlenberg² and found to be 0.195 volt, the alcoholic pole being positive. To determine the solution-tension of the zinc in the alcoholic solution, we must know the dissociation of the one-tenth normal solution of zinc chlo-

¹ J. Phys. Chem., 3, 400.

² *Ibid.*, 3, 389.

ride in ethyl alcohol. This will be seen from the following equation for the electromotive force of the above cell :

$$-\pi = \frac{0.058}{2} \left(\log \frac{P_1}{p_1} - \log \frac{P_2}{p_2} \right),$$

in which P_1 and P_2 are the solution-tensions of zinc in the alcoholic and aqueous solutions, respectively, and p_1 and p_2 the osmotic pressures of the zinc ions in the alcoholic and aqueous solutions.

In the above equation P_2 and p_2 are known, π was measured, and we must therefore know p_1 before we can calculate P_1 .

We have a method for measuring approximately p_1 —the dissociation of zinc chloride in ethyl alcohol—at a concentration of one-tenth normal. The boiling-point method which has been improved and used by one of us¹ to measure dissociation, was employed.

The zinc chloride which we used was prepared by distilling a fine sample of zinc chloride in a hard-glass tube through which a stream of hydrochloric acid was passed. This was done to remove any oxychloride which might be present, or which might be formed when the last traces of water were being removed from the zinc chloride. The redistilled zinc chloride was allowed to cool in the glass tube in the stream of hydrochloric acid gas, and was then removed to a desiccator and kept over phosphorus pentoxide. The salt thus quickly lost every trace of the acid gas which clung to it when it was removed from the glass tube.

The ethyl alcohol used was dried first over lime, and after distillation was kept over copper sulphate for several months. A solution of zinc chloride in ethyl alcohol of the strength desired ($\frac{N}{10}$) was prepared, and with this the dissociation of the solution was measured.

The mean of six determination showed that a tenth-normal solution of zinc chloride (by volume) in ethyl alcohol is dissociated 6.5 per cent. It seems probable from our determinations that this is correct to within 1 per cent. Substituting this value of p_1 in the equation :

¹ *Loc. cit.*

$$-\pi = 0.029 \left(\log \frac{P_1}{p_1} - \log \frac{P_2}{p_2} \right),$$

and solving for $\log P_1$, we have:

$$\log P_1 = -\frac{\pi}{0.029} + \log P_2 + \log p_1 - \log p_2.$$

$$P_1 = 1.9 \times 10^{19}.$$

We have calculated the solution-tension of zinc in an alcoholic solution of zinc chloride by a second method. Kahlenberg¹ measured also the absolute electromotive force of the alcoholic side of the above element, by means of a standard electrode, and found it to be 0.327 volt.

The equation for the potential upon the alcoholic side of the cell is:

$$\pi = 0.029 \log \frac{P_1}{p_1},$$

the symbols having the same significance as in the last equation.

$$\log P_1 = \frac{0.327}{0.029} + \log p_1.$$

$$P_1 = 2.7 \times 10^{10}.$$

The values of P_1 , calculated by the two methods, agree as well as could be expected. *Hence the solution-tension of zinc in ethyl alcohol equals, approximately, the solution-tension in water divided by 10^8 .*

In determining the value of p_1 by the boiling-point method, the assumption is made that zinc chloride in ethyl alcohol is dissociated to the same extent at the boiling-point of the alcohol, as at ordinary temperatures. This assumption cannot be far from true, since it was shown several years ago² that dissociation in water, as measured by the freezing-point method at 0° C., agrees very closely with the dissociation as measured by the conductivity method at 18° C.

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¹ *Loc. cit.*

² *Ztschr. phys. Chem.*, 11, 529; 12, 639.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

NOTES ON LECTURE EXPERIMENTS TO ILLUSTRATE EQUILIBRIUM AND DISSOCIATION.

BY JULIUS STIEGLITZ.

I. Equilibrium and Gaseous Dissociation.

The prominent rôle played by conditions of ionic equilibrium in solutions of electrolytes makes a thorough presentation of the subject desirable in college courses on general chemistry, and a still more exhaustive study necessary in analytical chemistry. The relative size of the dissociation constants and the influence exerted on the condition of equilibrium by increasing the concentration of one of the dissociation-products are the points most emphasized. It seems desirable to impress these two points on the mind of the student at the stage where the general subject of equilibrium and dissociation is first dealt with, which may, perhaps, be done best in connection with the question of gaseous dissociation, raised, for instance, by the vapor-density determinations of phosphorus pentachloride, ammonium chloride, etc. The following two lecture experiments with phosphorus pentabromide and phosphorus trichloridibromide¹ were developed to illustrate the second of the two points mentioned, the effect of an increase of the concentration of one of the products of gaseous dissociation. The contrast of the tubes showing the dissociation of the pentabromide and the trichloridibromide at 50° may also serve to demonstrate the first point, the influence of the relative size of the dissociation constant or the relative ease of dissociation, in default of substances for which the constants for gaseous dissociation have actually been determined and which could at the same time be used for lecture experiments in general chemistry.

Phosphorus Pentabromide and Phosphorus Tribromide.

The effect of an excess of phosphorus tribromide on the dissociation of the pentabromide is shown by comparing the in-

¹ Vide Wurtz's work on phosphorus pentachloride, Ber. d. chem. Ges., 3, 572.

tensity of the color of the bromine vapor in two tubes charged as follows:¹

Sealed bulbs containing 0.029 gram bromine (1 molecule) and 0.058 gram phosphorus tribromide (a little more than 1 molecule) were placed in a piece of thick-walled tubing² closed at one end, the tube drawn out to a capillary, the air exhausted to 30 mm. pressure, and the capillary sealed rather close to the tube, the rest of the capillary being bent into a loop. The tube charged in that way was 18 cm. long and had a capacity of 40 cc. By vigorous shaking the bulbs containing the bromine and tribromide were broken. A second tube of the same size was charged with 0.029 gram bromine (1 molecule) and 0.45 gram tribromide (9 molecules). A few coils of lead or fuse wire were wound around the lower part of the tubes.

The tubes, thus prepared, are suspended side by side in a tall beaker of water by means of the glass loops at the upper ends. A glazed white porcelain tile placed in a slightly slanting position behind the beaker makes the comparison of the colors easier. On heating, at 50° only a very slight color appears in the first tube (see below, phosphorus trichloridibromide), none in the second tube. From 80° to 90° the dissociation has progressed to the most favorable stage for comparison; the first tube shows a more intense color than the second one, which contains the excess of the tribromide, the color of the former being reddish-brown and opaque while that of the latter is reddish-yellow, through which the white of the tile can still be seen.

Phosphorus Trichloridibromide and Phosphorus Trichloride.

The difference in color between the two tubes in the above experiment will be sufficiently evident to most students, but perhaps not quite marked enough for the student whose judgment is still to be developed. By using phosphorus trichlor-

¹ Instead of using phosphorus pentabromide it was found more convenient to use the tribromide and bromine in molecular proportions, weighed in small bulbs blown at the end of capillaries. The weighing out of the exact quantities required was rapidly accomplished by weighing a bulb both on an analytical balance and on rougher scales. When by means of the latter the amount required in the bulb was very nearly adjusted, the final weighings were made on the sensitive balance, the bulb being placed in a pair of weighing tubes fitting closely over each other.

² The ordinary tubing used for heating solutions under pressure.

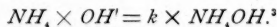
dibromide¹ with and without an excess of the trichloride greater differences in color were obtained, putting the student in question out of temptation to rely less on his own judgment than on the demands of theory.

Tubes of the same size (40 cc. capacity) were charged as above, respectively with 0.029 gram bromine (1 molecule) and 0.029 gram phosphorus trichloride (0.004 gram more than 1 molecule) and with 0.029 gram bromine (1 molecule) and 0.155 gram phosphorus trichloride (6 molecules); the air pressure in the tubes was reduced to 27 mm. At 40°-55° the difference in the colors of the two tubes is most marked, the first one being dark-brown and the second one yellow.

The influence of the relative size of the dissociation constants or the relative ease of dissociation of phosphorus pentabromide and of phosphorus trichloridibromide is shown by comparing, at 50°, the colors of the tubes containing these substances (the first tube in each series); the former is found to be nearly colorless, while the latter is dark-brown, showing the greater tendency of the trichloridibromide to dissociate.

II. *Equilibrium and Electrolytic Dissociation. Ammonium Hydroxide and Solutions of Ammonium Salts (Ammonium Ions).*

Lovén² has shown that the characteristic action of ammonium salts in preventing the precipitation of magnesium hydroxide by ammonium hydroxide is simply the result of equilibrium changes. The most important of these is the gradual suppression of the hydroxyl ions of the ammonium hydroxide by greatly increasing the concentration of the ammonium ions on adding the easily dissociating ammonium salts, equilibrium being established according to



This important action of ammonium salts can be demonstrated

¹ Phosphorus trichloridibromide dissociates at 35° into phosphorus trichloride and bromine (Michaelis: Ber. d. chem. Ges., 5, 9).

² Ztschr. anorg. Chem., 11, 404.

³ At the same time $NH_4OH = k' \times NH_3 \times H_2O$; the symbols are used to designate concentrations.

very simply by the following experiment¹ with phenolphthalein; after producing a brilliant red color by adding a drop or two of dilute ammonia to each of two beakers containing water and a little phenolphthalein, a few drops of a rather concentrated solution of ammonium chloride are added to the contents of one of the beakers. The color fades to a scarcely perceptible pink and then disappears.

As ammonium chloride is liable to have an acid reaction ammonia may be added to its concentrated solution until a little of it can be shown to give a faint but distinct pink color to a solution of phenolphthalein—proving that it certainly contains no free acid. On adding a few drops of this somewhat *alkaline* ammonium chloride solution to the crimson solution produced by a drop of ammonia, the red color instantly gives way to a faint pink. This form of the experiment seems to be the most convincing and striking one: the adoption of either form must depend on the advancement of the class.

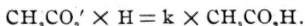
It may be added that ammonium chloride solutions which react distinctly *alkaline* to litmus (see below) make the red color produced by the action of ammonia on phenolphthalein disappear completely. These experiments are, of course, based on the well-known lack of sensitiveness of phenolphthalein towards hydroxyl ions.

With analytical students the experiment just described may well be followed by a parallel experiment with litmus solution: it is best to use four beakers containing neutral litmus solution; the first is used to preserve the original tint; to the second 5 to 10 cc. of a concentrated ammonium chloride solution are added, which, to avoid the suspicion of acidity, has been made very slightly alkaline; the color in this second beaker changes distinctly towards a bluer violet. The other two beakers are each treated with a drop of quite dilute ammonia, which gives to each a pure-blue tint, and to one of them 5–10 cc. of the solution of ammonium chloride are added,

¹ The experiment may serve as a particularly simple and pretty illustration of ionic equilibrium in general and as a basis for the discussion of the use of ammonium salts with ammonia in many important reactions of analytical chemistry, *e. g.*, in preventing the precipitation of magnesium hydroxide and many analogous hydroxides, in facilitating the quantitative precipitation of aluminium hydroxide, etc. The simpler form is preferable for general chemistry classes, the use of the slightly alkaline ammonium chloride is more instructive for advanced students.

the color reverting to violet. The change is perfectly plain; but, as litmus is more sensitive to hydroxyl ions than phenolphthalein, the change is not as pronounced as when the latter is used.

Küster¹ has described a lecture experiment to show, by means of methyl orange, the analogous suppression of the hydrogen ions of acetic acid by adding acetate ions in the form of an acetate (*e. g.* sodium acetate), according to



In consequence of hydrolysis sodium acetate reacts alkaline and the experiment in its original form is, perhaps, open to this objection. A convincing and striking proof of its correctness may be given by using a solution of sodium acetate which, to prevent the suspicion of alkalinity, has been made very slightly acid, giving with methyl orange the well-known reddish-brown hue of beginning acidity. On adding even 2 or 3 drops of this slightly acid solution to a beaker of a methyl orange solution, colored an intense red by a drop or two of acetic acid, the red color is at once replaced by the brown hue of lesser acidity.

CHICAGO, February 19, 1900.

A CONTRIBUTION TO THE KNOWLEDGE OF TELLURIUM.

BY F. D. CRANE.²

The rise of the electric refining industry has placed within reach the dross which is produced in large quantities in the final purification of the precious metals, and it is with tellurium from this source that the work here described was done. The process by which the by-product is obtained has been described by C. Whitehead.³ It contains much silica, tellurium mostly as tellurite, with a little tellurate due to the drying, and some selenium, antimony, arsenic, copper, and

¹ Ztschr. Elektrochem., 4, 110.

² From the Author's dissertation for the degree of Doctor of Philosophy, submitted to the Board of University Studies of the Johns Hopkins University, June, 1898. The work described was undertaken at the suggestion of Professor Remsen and carried on under his supervision.

³ J. Am. Chem. Soc., 17, 849.

other metals. Varying quantities of iron and aluminium and a relatively large quantity of potassium are present.

Extraction of Tellurium.

From this white substance the tellurium is readily extracted by repeated leaching of the powdered material with strong commercial hydrochloric acid. Heating the acid does not appear to be of much advantage. The best results are obtained when large quantities of it are used.

In order to filter the slimy mud at all rapidly, a good pump and as large a filtering surface as possible, should be used. To make such a surface a 3.5 cm. Witte plate is put in a large funnel and covered with a rather thick layer of glass beads. On this is placed a layer of asbestos in the usual manner. This device allows lateral passage of the filtrate, and gives a much larger effective surface than the combined area of the holes of a plate alone.

The bright-yellow hydrochloric acid solution which is obtained is evaporated to a convenient consistency, depending on the use to which it is to be put. It contains considerable quantities of the metals which occur as impurities as well as the tellurium and selenium.

Precipitation of Tellurium.

Since the work of Berzelius the use of sulphur dioxide as a precipitant of tellurium has ordinarily been advised, although it has been known equally long that the action is never quite complete and that traces of other metals, as well as all the selenium, come down also. Its exceeding convenience, however, was a strong reason for its use in the present instance for at least the preliminary precipitation. It was found that, in all probability, the main reason for the incompleteness of its action is the very rapid increase in the ratio of acid to unprecipitated tellurium in the solution, two-thirds of this being due to the hydrochloric acid set free, and one-third to the sulphuric acid formed.

If these could be removed the precipitation should go on. Evaporation sufficed for the hydrochloric acid, and an addi-

tional quantity of tellurium was obtained, but the increase of the sulphuric acid soon stopped the reaction.

The practical removal of the acids by neutralization was then tried, and it was found that the addition of an alkali or alkali carbonate resulted in a renewed precipitation. At this point Mr. R. L. Whitehead advised the use of acid sodium (or potassium) sulphite; and his suggestion was thenceforward followed.

But even with this very efficient reagent the action in the cold is never quite complete. It was found that, if a solution in which neither more acid sulphite nor more hydrochloric acid, added to decompose some of the excess of acid sulphite already present, will produce a further precipitate, is heated to boiling, there is then a further precipitation without any addition of reagents.

It is better to remove the first precipitate before boiling, as the action is then more readily seen. This new precipitate gives the qualitative reactions for tellurium, and differs from the first precipitate only slightly in tint. Its formation is probably due to the decomposition of some alkali tellurate at first formed through mass action. By this means, then, the tellurium was obtained, mixed with selenium and a little of the other impurities.

Precipitation of Tellurium by Magnesium.

In devising a method for the more accurate estimation of tellurium it was found that metallic magnesium would completely precipitate tellurium from a solution of the tetrachloride in hydrochloric acid. The excess of hydrochloric acid should be as small as possible, and a slight excess of magnesium should be added. This latter may be destroyed by vigorous boiling, when it decomposes the water; the magnesium hydroxide is then removed by acidifying very slightly with acetic acid. The well-washed tellurium precipitated by this method seems to be less easily oxidized.

Detection of Tellurium.

The apparent completeness of the action of acid sodium sulphite led to the idea that it would detect small quantities

of tellurium and do this more rapidly and efficiently than former methods. To test this, a weighed portion (0.107 gram) of tellurium was dissolved in hydrochloric acid by the aid of as little chlorine gas as possible, and the solution gently heated to expel any excess of chlorine. It was then diluted with a little hydrochloric acid and finally with water to 500 cc. Ten cc. of this solution gave a marked precipitate. Ten cc. were diluted to 110 cc., and as the same quantity of this also gave a strong reaction, the dilution was repeated in a similar manner. An effective surface of about one-half a square centimeter of white filter-paper was used to collect the precipitate, and on this the layer of black tellurium was plainly visible; the amount present per cubic centimeter of solution being 0.00000214 gram, and the total quantity used being 0.0000214 gram. The presence of tellurium was still discernible when the dilute solution contained only 0.000000214 gram per cubic centimeter and there was present but 0.00000214 gram.

It appears probable that this limit is due simply to the fact that we have here nearly reached the physiological limit of seeing black on white.

Detection of Selenium.

Mr. Edward Keller has recently called attention to the precipitation of selenium by ferrous sulphate,¹ and this reaction was tested in like manner, 0.1139 gram of selenium being weighed out, dissolved, and diluted. The precipitated selenium colored the paper the bright, characteristic red when the dilution was 0.00000207 gram per cubic centimeter, ten times that quantity being used. And at a dilution of 0.000000207 gram per cubic centimeter the precipitate from 10 cc. was more easily seen than that of tellurium at about the same dilution.

Furthermore, the precipitation of selenium at a dilution of 0.00000207 gram per cubic centimeter is independent of the presence of a little more than one hundred times as much tellurium as tetrachloride.

Precipitation of Tellurium by Ferrous Sulphate.

Mr. Keller² states that ferrous sulphate does not precipitate

¹ J. Am. Chem. Soc., 19, 771.

² Keller: *Loc. cit.*

tellurium. The statement is evidently made with respect to a solution of the tetrachloride in hydrochloric acid, and, if only the tetrachloride is present, it is quite true. Ferrous sulphate, however, precipitates tellurium from a solution of the tetrachloride in hydrochloric acid if it has been boiled vigorously for some time, the evaporating acid being replenished; or if it is boiled, heated, or remains for some time in contact, with tellurium.

This seems to be due to the presence of tellurium dichloride. But tellurium dichloride, according to Rose,¹ breaks down in the presence of acids into tellurous acid and tellurium. To test this the two chlorides of tellurium were made, first by the direct action of chlorine on tellurium, and then by the action of this tetrachloride on the proper amount of tellurium. The solution which was obtained by treating the dichloride in the cold with hydrochloric acid gave, to a slight extent, a black precipitate with ferrous sulphate, and a solution made with the hot acid gave it much more markedly.

A mixture of the two chlorides treated with the acid gave a very decided precipitate, and a solution of the dichloride in a strong solution of the tetrachloride in hydrochloric acid, gave it most strongly of all. In all these experiments the known decomposition of the dichloride into free tellurium was prominent and evidently nearly in theoretical quantity, so all the solutions were well filtered before the ferrous sulphate was added.

The actual mass of the precipitated tellurium is small in comparison with the quantity present as chloride, but the deep black color and the very fine state of division produce a very marked effect. The black precipitate collects and settles after a time, and seems to diminish in bulk.

This is no doubt the same sort of change as that which occurs in tellurium precipitated by sulphurous acid or acid sulphite, and that is probably akin to the changes in precipitated selenium and tellurium when heated.

Furthermore, a boiling solution of tetrachloride in hydrochloric acid will dissolve a little tellurium. In order to have the action complete, there must be but little of it, and that in

¹ Rose: *Pogg. Ann.*, 21, 443.

a state of fine division. This action may account in part for the apparent diminution of the precipitate just mentioned.

It is hard to keep a concentrated solution of the chloride in a condition in which it gives no precipitate with ferrous sulphate, but it may be quickly brought to such a condition by passing through it a few bubbles of chlorine, the excess of which is soon lost by allowing the solution to stand open a short time.

Purification of Tellurium.

The purification of tellurium in quantity appeared to be a question of getting rid of selenium on the one hand, and of various more metallic elements on the other. And it seemed advisable to do this as simply as possible in view of the uncertainty as to the individuality of the substance.

Suspicion has been cast, at various times, on all methods which require repeated evaporations, distillations, or crystallizations, or in which nitric acid must be removed by prolonged heating. Further, it has been directly alleged that distillation in hydrogen gave a product with a lower relative weight.¹

The method of Keller works well for selenium, if precaution is taken to prevent a reversal of the action through the mass action of the tellurium tetrachloride on the precipitated selenium, which will be referred to below. But it has the great disadvantage of burdening the solution with iron salts and sulphuric acid, which latter always makes the precipitation of tellurium more difficult.

The method of Stolba,² which depends on the reduction of a tellurate in alkaline solution by boiling with glucose, which reduction is claimed to begin and be completed before a similar action with any selenite present, appears to work as described. But in the presence of the excess of glucose and its decomposition products it is very hard to determine the limits of the reactions. Pure tellurium is unquestionably formed at first, but the uniformity of the reaction remained in doubt. This process could doubtless be made to work well, but it was not used, since that to be described seemed simpler.

¹ Bauner: J. Chem. Soc., 55, 392.

² Stolba: Jahresbericht, 1873, 214.

As only a small fraction of the more metallic elements was carried down by the tellurium, it seemed probable that several precipitations would remove practically all of these. Consequently, it was required to repeatedly convert the precipitated tellurium into the tetrachloride. The direct action of gaseous chlorine on dry tellurium is very rapid, but much heat is evolved, enough, in fact, to volatilize a part of the chloride unless the process is carried on quite slowly. The action of gaseous chlorine on tellurium suspended in strong hydrochloric acid is, on the other hand, quite slow; and rapidly becomes slower as the quantity of dissolved chloride increases, and is very slow if the tellurium is at all compact.

It has long been known that tellurium is much more metallic than selenium, and that selenium is the first to be precipitated by sulphur dioxide. In fact this method has been suggested for their separation. Now it seemed probable that, if the mixed precipitate could be subjected to the action of nascent chlorine, by being made the positive pole of an electrolytic cell containing hydrochloric acid, not only would the tellurium be rapidly converted into the chloride at a low temperature, but also the more metallic tellurium would be first attacked, to the practical if not total exclusion of the selenium.

Preliminary trials on a small scale having shown the rapid action of the nascent chlorine, a larger apparatus was made. This consisted of a 750 cc. funnel with the stem ground square off. In the bottom of the funnel portion was placed a button of commutator carbon about 2.5 cm. in diameter, to which was soldered a small brass nut.

The button was sloped to fit the funnel and jacketed with a doubled rubber tube. Through the stem of the funnel was passed a heavy copper wire, threaded at both ends, and having on the lower end a small nut. The upper end of this wire was screwed into the nut on the button, and the button then drawn down tight by the lower nut acting against the lower end of the funnel stem. This formed the positive pole, the current being taken in on the wire.

The negative pole was formed of a sheet of thin copper of some 30 sq. cm., which was soldered to a convenient wire.

This pole was never in the acid but a moment before the current was on, and was removed at once when it was off, so that it was not attacked by the acid. To prevent the deposition of tellurium, it was inclosed in a little porous cell which was hung on the edge of the funnel. A small automatic drip supplied pure hydrochloric acid just fast enough to keep the surface of the liquid in the cell about 0.5 cm. above that in the funnel, so that there was always a flow of pure acid through the cell away from the negative pole. It was expected that the sloping sides of the funnel would keep the unattacked tellurium always at the bottom, but as the specific gravity of the solution increased, the solid did not sink rapidly enough, so a glass rod, mechanically turned, was put in to act as a stirrer. When somewhat heated from the passage of the current, this arrangement had a very constant resistance of a little more than half an ohm, and, with the current employed, used about 9 amperes.

Practically, every trace of the chlorine liberated was absorbed, and consequently the speed of solution depended directly on the current. The first charge of the cell was not quite all dissolved when it became necessary to stop the action over night, and the entire contents of the cell were removed to another vessel. At the same time a portion of the liquid was taken out and tested for selenium, which was found to be present. Evidently the tellurium was not exclusively or primarily attacked, as some of it visibly remained. The next morning this test was repeated, and no selenium was found. And the reddish color of the selenium indicated that it had been precipitated. This electrolytic chlorine method of solution is very efficient and has the marked advantage of adding no foreign substance. It is the more rapid, of course, the more finely divided the tellurium.

Separation of Selenium by Tellurium.

Further experiments showed that if to a mixture of selenium dichloride, and tellurium tetrachloride dissolved in hydrochloric acid, tellurium is added, or a portion of the tellurium precipitated, and the mixture allowed to stand for some time, or better and much more expeditiously, boiled, all the

selenium will disappear from the solution, and will be found in the sediment, with the excess of tellurium. If the action takes place at the ordinary room temperature, the selenium can easily be seen on account of its color, but if heat is used the well-known change to the black form will occur, and it cannot be distinguished from the tellurium.

It can be readily detected, however, by filtering off the black residue and dissolving it in a little hydrochloric acid by the aid of chlorine, when the selenium may be again precipitated. If this reaction is carried on upon a microscope slide, it can be well seen and makes a very pretty effect when magnified to about 80 diameters.

On the large scale it is preferable to heat the solution of mixed chlorides gently just below the boiling-point, and to have the tellurium in as fine a state of division as possible and well mixed with the fluid. To attain both these ends it is advisable to precipitate some of the tellurium, either by leading in a little sulphur dioxide, or adding a little acid sulphite. The turbid liquid which results does not clear for some time by settling.

That this process is complete is shown by the fact that it not only removed selenium from tellurium tetrachloride solutions so completely that none could be detected by the ferrous sulphate test, but also removed selenium completely from a solution of selenium dichloride in hydrochloric acid, previously precipitated tellurium being employed. In this experiment tellurium is found in solution which shows conclusively a replacement or an exchange.

If, on the other hand, selenium is gently heated in a solution of tellurium tetrachloride for some hours, the addition of ferrous sulphate to the filtered fluid will show that a very small part of the selenium has gone into solution. This minute amount may be entirely removed by the treatment with tellurium. This seems to explain the observation that in working with quite large quantities of the mixed chlorides in solution, the action of ferrous sulphate even in excess did not seem to be quite complete if a few hours elapsed before the precipitated selenium was filtered off. But the solution could not be made to take up selenium if there was a little

tellurium present, and it was kept well stirred. The phenomenon appears to be, to some extent at least, one of mass action.

In using this process for the removal of selenium, the precipitate, containing the excess of tellurium, is filtered off and redissolved, either by nascent chlorine or by conducting into it, suspended in hydrochloric acid, a stream of that gas. The selenium is then easily removed by ferrous sulphate and the tellurium by acid sulphite. It is well to avoid the use of nitric acid.

The Further Purification of Tellurium.

The logical sequence to boiling the mixed chlorides with tellurium in order to precipitate selenium or any less metallic elements was to boil the precipitated tellurium with a reserved portion of that solution from which it had been obtained, so that any more metallic elements which might have been carried down would be dissolved, and precipitate an equivalent quantity of tellurium. This was done, although several precipitations in the ordinary manner seemed to have already removed those traces of metals which have been previously noted as occurring in the crude material.

The tellurium prepared in this manner has the usual appearance and reactions, and could be completely distilled in a current of hydrogen, leaving only a slight residue of carbonaceous material probably derived from the filter-papers. It was noted that there was very little tendency to form hydrogen telluride with pure, dry hydrogen.

This process should tend to separate the suspected homologue of tellurium of greater relative weight, and although no definite indications of such a substance have been met with up to the present, work will be continued along this line if time and opportunity are found.

Determination of Tellurium.

There has never been any sure method of determining tellurium. Most observers have either determined other elements in the tellurium compounds, or precipitated the tellurium, treated it with nitric acid, and converted the compound

thus formed into the dioxide by heat. This has been the most exact method.

But Brauner¹ notes the brown decomposition which Staudenmaier² had observed, and further claims that the nitric acid is not wholly driven off before a part of the dioxide is volatilized. A method of avoiding the brown color has lately been given by Norris and Fay,³ but nothing is said as to the removal of the nitric acid, and there is visible volatilization. But gravimetric determinations by the method about to be described showed that the dioxide prepared by that method was quite pure. However, it is doubtful if nitric acid can be removed without some volatilization.

No volumetric method which does not require a correction term, with the exception of that of Norris and Fay, has been devised. The objections to the direct precipitation and weighing of the tellurium were alleged to be two: that it was not possible to precipitate all the tellurium from an acid solution, and that after precipitation it was oxidized so much in drying that the results were variable.⁴

In view of the extreme delicacy of the acid sodium sulphite as a test for tellurium, it seemed advisable to try it as a precipitating agent in quantitative work. There is no doubt that free acid does prevent the complete action of sulphur dioxide, but there is no evidence that neutral alkali salts in solution do this, if the solution is heated; at least qualitative experiments failed to show such an action. So it is only necessary to add enough acid sulphite to give up soda to the acids present and set free. A slight excess of sulphite does no harm, and an excess of sulphur dioxide is readily removed. After the acid sulphite has been added, it is advisable to let the mixture stand for a time, usually, for convenience, over night, as the precipitate seems to be in better mechanical form when this is done. But the action may be completed at once by heating. At any rate, the liquid with the precipitate still in it should be raised to the boiling-point for a short time. This is to gain two ends: to insure the total

¹ Brauner: *Loc. cit.*

² Staudenmaier: *Ztschr. anorg. Chem.*, **10**, 206.

³ Norris and Fay: *This JOURNAL*, **30**, 278.

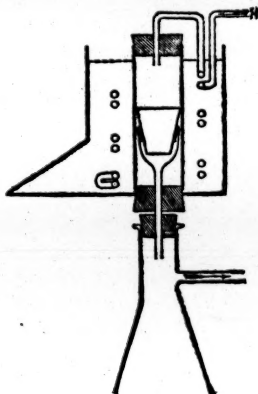
⁴ Brauner: *Loc. cit.*; Norris and Fay: *Loc. cit.*

precipitation of the tellurium, which is never quite complete in the cold when large amounts are being handled (as has been noted); and to cause some definite but undetermined change in the precipitate. As a result of this it becomes much easier to filter and wash, and less liable to oxidation. This change, as has been said, seems to be like the long-known change in selenium. It is hard to describe, but easily recognized, although it consists only of the merest change in tint and a difference in the manner in which the precipitate settles. The precipitate is then collected on a Gooch filter and very thoroughly washed, care being taken that it always shall be covered with water. If speed is more requisite than exactness, it may now be pumped as dry as possible, quickly dried in an air-bath, and weighed. It will oxidize to some extent, but by no means seriously. The oxidation can easily be detected and the extent of it quite accurately judged by removing the precipitate with the filter surface, after weighing, and putting it in a beaker on a white surface, or in an evaporating dish and moistening it with a few drops of strong hydrochloric acid. A yellow tint of dissolved chloride appears at once only if oxidation has occurred, as unoxidized tellurium does not color hydrochloric acid. But if this preparation is allowed to stand, a color will appear, as the air acts readily on the acid mud. To determine how far this color could be used as a criterion of the presence of oxide and its amount, a weighed portion, 0.0068 gram, of pure tellurium tetrachloride was dissolved in strong hydrochloric acid and diluted. The yellow color of a layer 0.25 cm. thick was plainly visible when 0.00013 gram of tetrachloride was present in each cc.

To see if the method without special precautions in drying was even nearly correct, portions of a pure precipitated tellurium in which very little oxidation had occurred were weighed out, dissolved in a little hydrochloric acid by the aid of chlorine gas and treated as stated above.

Taken. Gram.	Found. Gram.	Gain. Gram.	Recovered. Per cent.
0.1768	0.1779	0.0011	100.6
0.1285	0.1289	0.0004	100.3

Probably practice in its use would make this method exact enough for all practical purposes. From the article by Mr. Keller already referred to, it appears that no special precautions in drying are used at the works of the Baltimore Electric Refining Company.



Device for Filtering.

To prevent, if possible, any oxidation, the filtering crucible was enclosed in a cylinder through which dry, pure hydrogen which had just been passed over hot platinized asbestos was slowly drawn under slightly diminished pressure. The device was so arranged that it was not necessary to remove it from the filter flask, and a T-tube in the pump connection was joined to a mercury safety-valve by which both the pressure and flow were regulated. The cylinder and its contents were heated by jacketing them with a strong solution of calcium chloride, after the manner of a hot-water funnel, and this bath was also used to warm the entering stream of hydrogen.

This arrangement prevents oxidation as far as can be detected by the coloration of hydrochloric acid, and as the results seem quite constant, it probably does not occur to a measurable extent. There is no evidence to show that tellurium, which has been boiled with water, can decompose water

in the presence of hydrogen, so that the essential thing is to have pure hydrogen.

The Method.—The entire process is as follows: The given compound is so treated that the tellurium is in the form of the tetrachloride, avoiding, if possible, the use of nitric acid, and as little hydrochloric acid as possible being used. The solution is now diluted with water, but not to such an extent that a white substance appears, although a little of this seems to do no harm. The objection to a larger quantity is mechanical, the interior of the flocculent masses seeming sometimes to be unattacked by the sulphuric acid. A solution of acid sodium or potassium sulphite is now added. It should be moderately concentrated, and the quantity should be such as to neutralize nearly exactly the acids present and set free by the base of the reagent. The excess of sulphur dioxide will escape harmlessly, but anything more than a slight excess of the acid sulphite is detrimental. The mixture, which has turned dark, has been gently agitated during these manipulations; it is now diluted to about 50–75 cc. and allowed to stand for a time as the precipitate thus seems to form more evenly. But it may be warmed at once.

If too much sulphite has inadvertently been added, the precipitate should be decanted and reserved, and the precipitate washed once or twice and the decanted wash-water added to the other, and all this passed through the weighed filter later. The reason for this is that it is very hard to decant without getting some of the precipitate over, although it may remain invisible until it blackens the filter. If time is not a consideration, this decantation process may well be employed in all cases.

The precipitate, in about 75 cc. of water, is now gently warmed, being stirred with a glass rod tipped with a bit of rubber tube, both to prevent "bumping" and to detach those portions which at times form a very marked "mirror" on the sides of the vessel; it is allowed to boil rapidly for a moment or two, and then set aside. A little water may be added, as it aids the settling. The tellurium, which has changed in appearance, should settle very quickly. If it does not, it may be boiled a little more, but it is to be noted that differ-

ences in the concentration of the solution in which the precipitation took place may markedly influence the character of the precipitate.

The amount of material taken should be such that the tellurium will form a rather thin layer in the filter even while still wet. The precipitate is now filtered through a weighed filter, care being taken to keep it always covered with water, and well washed, and since there is no reason to suspect any action of the water, the washing should be thorough.

After the washing is completed, the hydrogen supply is connected at once, the last water being followed through the filter by the hydrogen. But no effort need be made to displace the small amount of air in the cylinder.

The temperature of the calcium-chloride bath is now quickly raised to about 110° and kept there till the tellurium is dry. This must be judged from its appearance.

The filter is then removed to a desiccator, and, when cool, weighed. There is no tendency to oxidize rapidly in the air if thoroughly dry. The main danger to be avoided is the accidental access of air to the wet tellurium.

Some of the results obtained by this method are as follows:

Tellurium Dioxide from the Nitrate, Te = 127.6; O = 16.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.1047	0.0838	79.95	80.03
0.1130	0.0904	79.95	80.00

Tellurium Tetrachloride Distilled in Carbon Dioxide, Cl = 35.5.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.3879	0.1857	47.33	47.87
0.5678	0.2717	47.33	47.85

Tellurium Oxychloride, Fused.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.62075	0.3689	59.46	59.43

Tellurous Acid, from the Chloride.

Taken. Gram.	Found. Gram.	Required. Per cent.	Found. Per cent.
0.11985	0.0862	71.84	71.92

A Yellow Form of the Dioxide.

If a solution of tellurium tetrachloride in hydrochloric acid which has stood for some time after the selenium has been precipitated by ferrous sulphate and removed, or a similar solution to which ferrous or ferric chloride has been added, is diluted with water, a white precipitate is formed. If this is now allowed to stand for a time, the excess of water being decanted and replaced till it is not colored by the iron, a heavy yellow precipitate will appear. Or if the solution is poured directly into boiling water, the whole mass or precipitate will be colored yellow. The difference in specific gravity is so great that the remaining white substance may be almost completely removed by washing.

This substance is easily soluble in hydrochloric acid, and more difficultly in nitric and sulphuric acids. It is readily and completely dissolved by alkalies and forms a colorless solution without residue. Under the microscope it is seen to consist of more or less regular yellow crystals, of the isometric system, octahedrons, sometimes modified by cubic faces. Among these were traces of a white substance which seemed to cling to the crystals. It appears to be a form of tellurium dioxide, analyses giving the following percentages of tellurium: 79.46, 79.52, 79.51, 79.58, 79.46; calculated for TeO_2 , 79.95. The discrepancy may be due to the adherent white substance, or to a little iron, of which a trace may be found by the ferrocyanide and sulphocyanide tests. To this also may be due the yellow color, which is very persistent, not yielding to nitric acid till the substance is all in solution, but the solution is colorless and deposits white crystals.

Decomposition of the Tetrachloride.

If water is added to a portion of the distilled tetrachloride of tellurium, considerable heat is evolved and it passes into solution as a yellow liquid. If more water is added a curdy white substance is formed, which settles and after a time forms the crystalline dioxide. The white substance is tellurous acid, but the wash-water from it constantly contains a trace of chlorine, and there may be a little of some sort of oxychloride present. But if there is also present another

metal, as iron, and particularly if antimony or arsenic is present, there is a marked change in the character of the white substance. It remains unchanged in water for days, and may be washed, dried, and redissolved and reprecipitated several times without forming the dioxide; and no fixed amount of tellurium was found in various samples. It appears to be a double oxychloride, and will be the subject of further investigation, if possible.

Failure to Form Analogues of Thiosulphate.

The attempt was made to form substances analogous to thiosulphates by boiling sodium tellurite with sulphur, selenium, and tellurium, but after several hours no trace of any action could be found.

Instability of the Chlorides.

Many minor observations, as well as those already noted, show that the chlorides of tellurium tend to pass to a slight extent from one to the other. This is especially true of the tetrachloride, which darkens when distilled in dry carbon dioxide. It is to this that the high percentage of tellurium noted above is probably due. And even that distilled in chlorine will give a slight cloud with ferrous sulphate if it has been kept for a time.

Conclusions.

Tellurium may be easily obtained from certain wastes of electric refineries by extracting with hydrochloric acid and precipitating with acid sodium sulphite. Magnesium will also precipitate tellurium, and has some advantages for qualitative work, and also for quantitative. Tellurium may be detected in very dilute solutions by acid sulphite, and ferrous sulphate is equally sensitive with selenium, and is independent of tellurium tetrachloride. But ferrous sulphate precipitates tellurium under some circumstances, probably because some tellurium dichloride is present in the solution.

In order to avoid certain sources of suspected error, and to add nothing but hydrochloric acid as reagent, a method of dissolving tellurium by electrolytic chlorine was devised, and was found to work rapidly and well.

While using this it was found that tellurium would remove selenium. The use of tellurium for this purpose rather than any other reagent is of advantage because it does not add any other elements to the solution, or permit the escape of any portion of the tellurium beyond control. This replacement method may be extended to remove elements that are more metallic.

Tellurium can be estimated by precipitating with magnesium or acid sodium sulphite, boiling, drying in hydrogen, and weighing as tellurium.

The decomposition of the tetrachloride by water is not a simple matter, and becomes much more complex if other metals are present. The pure tetrachloride gives tellurous acid which decomposes to tellurium dioxide.

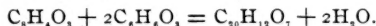
Contributions from the Chemical Laboratory of Cornell University.

THE CONSTITUTION OF GALLEIN AND COERULEIN.

[PRELIMINARY ARTICLE.]

BY W. R. ORNDORFF AND C. E. BREWER.

Although gallein was the first of the phthaleins discovered by von Baeyer, comparatively little work has been done on it and its derivatives. Baeyer's work¹ established the fact that gallein is the phthalein of pyrogallol, being formed from phthalic anhydride and pyrogallol in accordance with the following equation :



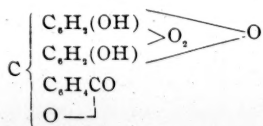
To gallin, the reduction-product of gallein, Baeyer gave the composition $\text{C}_{30}\text{H}_{18}\text{O}_7$, while to coerulein, the product formed from gallein by the action of concentrated sulphuric acid, he gave the formula $\text{C}_{30}\text{H}_{10}\text{O}_7$, regarding it as formed from gallein by the loss of hydrogen.

In 1881, after Baeyer had determined the constitution of fluorescein and phenolphthalein, Buchka,² at Baeyer's suggestion, took up the question of the constitution of gallein

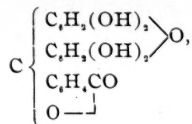
¹ Ber. d. chem. Ges., 4, 457, 555, 663 (1871).

² *Ibid.*, 14, 1326; Ann. Chem. (Liebig), 209, 249 (1881).

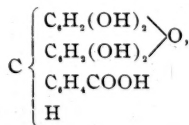
and coerulein. He states that gallein, when reduced in alkaline solution in the cold with zinc dust, gives a product, which he called hydrogallein, having *no acid properties* and yielding a tetracetyl derivative *identical with that obtained from gallein itself*. On further reduction this hydrogallein, according to Buchka, gives gallin, having acid properties and being easily converted into the phthalidin, coerulein, by the action of concentrated sulphuric acid. On the basis of this work Buchka asserts that gallein contains a quinone group and assigns to it the following formula :



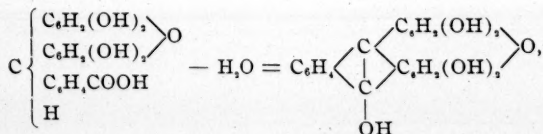
Hydrogallein formed by the reduction of the quinone group, according to him, has the following formula :



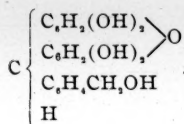
while gallin, the further reduction-product, is a true phthalin :



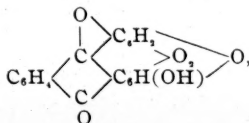
yielding the phthalidin, coerulein, with concentrated sulphuric acid, thus :



and gallol, on further reduction, to which he gives the formula :



For coerulein Buchka deduces the formula :



as it gives phenylanthracene, when heated with zinc dust, and a triacetyl derivative with acetic anhydride, just as gallein gives a tetracetyl derivative, by the reduction of the quinone group. No direct evidence of a quinone group in gallein is given by Buchka. It is assumed to be present, because, according to him, both gallein and hydrogallein give the same tetracetyl derivative, the identity of these products being proved by the fact that they have the same melting-point and give similar results on combustion analyses.

Some three and a half years ago we attempted to make hydrogallein and hydrogallein acetate in this laboratory by Buchka's method, but to our surprise we found it impossible to obtain these products. We repeated the experiment a number of times, following Buchka's directions to the letter, but always with the same result. The products we obtained were those called by Buchka gallin and gallin acetate. We then found, on looking through the literature, that Herzig¹ records a similar experience. He first made gallein acetate and found that it melted at 236°-237° C. Buchka gives the melting-point of his product at 247°-248° C. On reducing pure gallein with caustic potash solution and zinc dust, in the cold, according to the directions of Buchka, he obtained a product having, to be sure, the properties assigned by Buchka to hy-

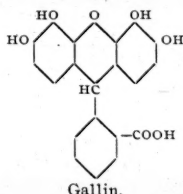
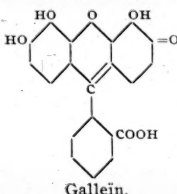
¹ Monatshefte für Chemie, 13, 426 (1892).

drogallein, but with acetic anhydride it gave *not gallein acetate, but a product melting at 211° – 213° C.*, and soluble in caustic potash solution without saponification, whereas gallein acetate is only soluble in caustic potash solution after saponification. Herzig states that this product is tetracetyl gallin, which, according to Buchka, melts at 220° C., though he did not make gallin acetate according to Buchka's method, for the purpose of comparing his product with it, but does call attention to the difference in the melting-points of the two products. Herzig was apparently not quite sure of his results, though realizing their importance for the determination of the constitution of gallein and coerulein, for he goes on to say: "Buchka scheint nach seiner Beschreibung eine grössere Menge des Hydrogalleins in der Hand gehabt zu haben, und es können daher meine beiden negativen Befunde vorläufig die Existenz desselben nicht in Frage stellen. Allerdings glaube ich, dass die Darstellung des Hydrogalleins nicht so einfach ist, wie sie Buchka beschreibt und dass noch andere Vorsichtsmassregeln nothwendig sind, die der genannte Autor entweder nur unbewusst eingehalten oder in seiner Arbeit zu erwähnen vergessen hat. Ebenso halte ich es vorläufig nicht für ausgeschlossen, dass die Identität der Acetylproducte des Galleins und Hydrogalleins nur auf Grund der Schmelzpunkte ausgesprochen wurde, während sie sich in Bezug auf die Löslichkeit in Alkalien von einander so unterscheiden können wie Acetylfluorescein von Acetylfluorescin." With this he leaves the subject.

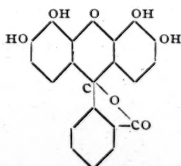
We had originally taken up the study of gallein with the idea that we might be able to contribute something to our knowledge of the constitution of the phthaleins. As, therefore, our results did not agree with those of Buchka on gallein, we resolved to repeat this work with great care. The Badische Anilin und Soda Fabrik of Ludwigshafen am Rhein, Germany, very kindly supplied us with all the gallein and coerulein which we used in this investigation, and we desire here to express our appreciation of their generosity and keen interest in our work. Our surprise may be imagined when we found that *not only did Buchka's hydrogallein and hydrogallein acetate not exist, but that the product which he calls gallol*

is in fact gallin. His hydrogallein, gallin, and gallol acetates are absolutely identical in every respect.

By making very careful analyses of the esters and ethers of gallein and gallin, we have found that the relations existing between these two substances are best expressed by the following structural formulas :



The hydrogallein, gallin, and gallol of Buchka are all the same and have the constitution given above for gallin. Gallein thus appears as the phthalein of pyrogallol as originally stated by von Baeyer, while gallin is the corresponding phthalin. That gallein has the above quinoid formula was shown by making a methyl and ethyl ester by boiling gallein with the corresponding alcohol and a little sulphuric acid ; by making the gallein triphenylcarbamate by heating gallein with phenyl isocyanate ; and by making the *colored* tetramethyl and tetraethyl ethers, which are easily saponified by sodium carbonate solution. Gallein also reacts according to the tautomeric form (lactoid formula) :

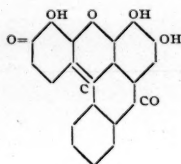


as it gives a *colorless* tetracetate, tetrabenzoate, and tetraphenylsulphonate. It also gives *colorless* tetramethyl and tetraethyl ethers. One particularly interesting derivative is the *colorless* trimethyl ether, which resembles phenolphthalein very closely. It dissolves in sodium carbonate or sodium

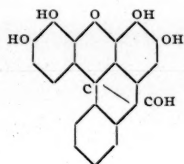
hydroxide solution with a red color, and is precipitated out *colorless* by acids. With acetic anhydride it gives very readily a *colorless* acetate (trimethyl gallein acetate), insoluble in alkalis. This same *colorless* trimethyl ether results from the saponification of the *colored* tetramethyl ether.

The constitution of gallin was proved by the fact that it gives a colorless tetracetate and pentamethyl ether. The gallin tetracetate has acid properties, as was shown by making a silver salt. The pentamethylether of gallin has no acid properties and is easily saponified.

We next took up the question of the constitution of coerulein and coerulein and found that they are best represented by the following structural formulas:



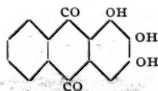
Coerulein.



Coerulein.

This was proved by showing that coerulein gives a triacetate, easily reduced in acetic acid solution with zinc dust, and coerulein, a pentacetate.

Buchka's statement that coerulein gives a tetracetate is incorrect. Coerulein thus appears as a derivative of anthragallol,



which, like coerulein, is soluble in alkalis with a green color. This will explain why coerulein resembles alizarin and anthragallol in its property of forming insoluble lakes with chromium, iron, and aluminium mordants. The name, alizarin green, by which coerulein is known, recalls this fact, which has been long known to the dyer. The above formula

for coerulein also serves to recall the aurin group of dyestuffs to which it shows certain resemblances.

Full analytical data supporting the views expressed in this paper will be presented later.

CORNELL UNIVERSITY, ITHACA, N. Y.,
March, 1900.

PERMANGANIC ACID BY ELECTROLYSIS.

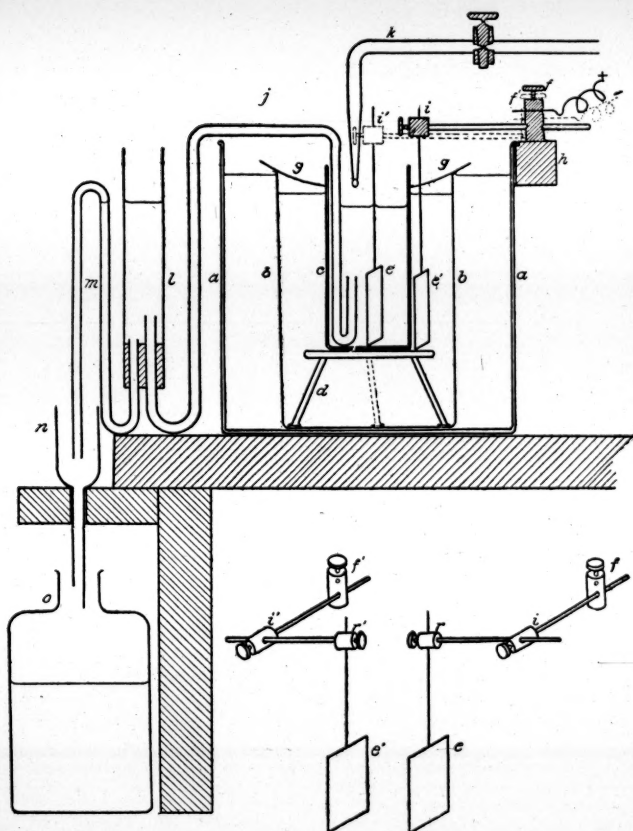
BY H. N. MORSE AND J. C. OLSEN.

In all of the work which has been done in this laboratory on the reduction of permanganic acid by manganese peroxide, the oxide has been prepared by partially reducing an acidified solution of potassium permanganate. But it is well known that the oxide, when precipitated in this manner, always contains a considerable quantity of potassium, and that it is not practicable to obtain an oxide free from alkali by increasing the excess of the acid which is added to the permanganate solution. The action of the oxide thus formed upon the unreduced permanganic acid, which has been the subject of our study, is doubtless influenced by the presence of potassium in the former. For this reason we desired to prepare an aqueous solution of pure permanganic acid, in order that we might obtain from it an oxide free from alkali or other bases. The need of such an acid was especially felt when we proposed to take up a study of the relative effects of equivalent quantities of sulphuric and nitric acids upon the evolution of oxygen which is produced by the oxide in solutions of the acid; for, if the oxide is made by the partial reduction of an acidified solution of the potassium salt, as has been our practice up to the present time, it is impossible to foretell in what proportions the potassium will distribute itself among the three acids; namely, that which is added, the permanganic acid, and the precipitated oxide. Nor is the case any clearer when the oxide is produced in neutral solutions to which an acid is afterwards added.

Two of the methods which have been employed hitherto appeared likely to yield a fairly pure acid. The first is by the decomposition of barium permanganate by sulphuric acid,

and the second, by the solution of the heptoxide in water. We decided to adopt the latter, and accordingly prepared a quantity of the anhydride by mixing potassium permanganate and concentrated sulphuric acid in vessels cooled by ice and salt. We soon learned, however, that something more than a low temperature is essential to safety in handling the product; for a minute quantity of the anhydride—certainly less than half a drop—which had been separated from the sulphuric acid, exploded with great violence and with disastrous consequences to one of us. We were unable to determine with certainty the cause of the explosion, but suppose it to have been occasioned either by accidental contact of the anhydride with some oxidizable matter or by slight friction between glass surfaces. Some idea of the force of the explosion may be gained from the fact that one of the flying fragments of glass passed entirely through a burette which was mounted in the vicinity, leaving holes over half the diameter of the burette, the edges of which were entirely free from cracks. After this experience, we decided to abandon the anhydride as a source of the acid, and to work out, if practicable, an electrolytic method of separating it from its salts. If a solution of a permanganate is electrolyzed in the usual manner, the acid is quickly reduced by the hydrogen which appears at the negative pole. This fact suggested the idea of placing the negative electrode in a porous cup filled with water, and of drawing off the accumulating alkali from time to time by means of a siphon. We pass over our earlier arrangements and preliminary experiments, and give at once the method which has already yielded us several kilograms of the acid in pure condition, and which appears to be adapted to its preparation in any desired quantity, whether for use in the free condition or for the manufacture of its salts.

The accompanying figure represents the apparatus which we employ: *a, a* is a galvanized iron tank through which hydrant water flows in order to prevent undue rise of temperature. We have in use two such tanks, each accommodating 5 cells. *b, b* is a beaker holding 1800 cc., in which are placed the permanganate solution, the positive electrode *e'*, and the porous cup *c*. The cup has a capacity of about 250 cc. and



rests upon the glass tripod *d*. It contains the negative electrode *e*, and one end of the siphon *j*. The open end of the siphon in the cup is on a level with the upper edge of the electrode. The electrodes are each 50 mm. square and are bent to conform to the sides of the cup; *e* is of silver and *e'* of platinum. *g* is a large watch-glass with a hole in the center equal to the outside diameter of the cup. It serves to collect and return the spray from the permanganate solution and to protect the latter from the dust in the air. *h* is a square wooden strip which is clamped to the edge of the tank. Into this are screwed the binding posts *f*, *f'*, etc. The arrangement by means of which the electrodes are made adjustable in all directions is more clearly shown in the supplementary figure. *k* is a glass tube with stop-cock through which distilled water is made to flow into the cup at any required rate, the rate depending, of course, upon the frequency with which it is desired to dilute the alkali by emptying the cup to the upper edge of the electrode. *j* and *m* are siphons connected in an obvious manner in the tube *l*. Through this system the alkaline solution in the porous cup empties into the bottle *o*, whenever its level rises above the upper bend in *m*. *m* empties each time completely, while *j* remains always full. The internal diameters of *m* and *j* should be related to each other about as 2 to 3. If they are equal, *m* will empty *l* and itself before the required amount of liquid has passed out of the cup, and will not again act until the cup has been re-filled.

The permanganate solution is made as concentrated as the temperature of the hydrant water which flows through the tank will permit. During the winter, the prevailing temperature of the water in the tanks has been from 10° to 11°; we have, therefore, employed solutions containing 40 grams of the salt in a liter. Owing to the destructive effect of the peroxide on the acid, the solution of permanganate should be filtered through asbestos.

Usually 8 or 10 of the cells described were arranged in series. As the current at our disposal was one of 220 volts, it was necessary to insert additional resistance. For this purpose, we employed 6 110-volt lamps, which were so installed

that the current could pass through any number of them in parallel; also so that any number could be thrown into series with any other number. On the average, about 40 per cent of the current was wasted in the lamps.

During the earlier part of the work, the current was broken at night and the cup removed from the permanganate solution. It was soon found, however, that when this was done the acid left in the walls was reduced in the interval, giving rise to a deposit of oxide, which greatly increased the resistance of the cup. In the later work, therefore, the current was uninterrupted from the beginning of an experiment to the end.

The resistance of the individual cells was determined twice daily; but, as it was subject to considerable temporary fluctuation—rising to a maximum whenever the cup was emptied by the siphon, and falling again as the refilling proceeded—the figures here given are to be regarded as having only a very general significance. As a rule, the cells were found to have a low resistance in the beginning, amounting to from 5 to 10 ohms on the first day. On the second day, it would rise to 25 or 30 ohms, only to decline through the third and fourth to perhaps from 10 to 14 ohms, after which the resistance remained fairly constant to the end. When the average of all the observations amounted to less than 13 ohms, the cup was regarded as a good one, though in some cases the average was below 9. The increase of resistance during the second day, and its subsequent decline to a minimum which was thereafter fairly well maintained, were characteristic of every experiment; but we could find no adequate cause for the phenomenon. Occasionally the resistance of a cell would rise much above 30 ohms, and would continue thereafter much higher than that of other cells in series with it. In such cases, the cups were replaced by others. On breaking them, their walls were found to contain a deposit of black oxide, which was always denser immediately between the electrodes than elsewhere.

The cup used by us was the ordinary porous battery cup; but, thinking that greater porosity might have the effect of diminishing resistance, and therefore of economizing current, we had made for us a number of new cups, in some of which

the clay was mixed with sand, in others with ground flint, and in still others with pulverized charcoal which was afterwards burned out. All of these were found to be more porous than the battery cups with which they were compared, but, as regards average resistance, they proved to be no better than the latter; while, in respect to yield of acid, the most porous of them were distinctly inferior. Those made from clay mixed with sand were too porous. The alkaline solution which was drawn from them was constantly colored in consequence of the infiltration of permanganate during the time that the cups were only partly filled. Usually, the alkali drawn from the other, less porous, cups was colorless. At times, however, when the refilling of the cups was slow—after having been partially emptied by the siphons—the inner exposed walls of even the less porous cups would take on a pink color from infiltration of permanganate. This was afterwards reduced, giving rise to a deposit of oxide on the walls or on the bottoms of the cups.

To test the relative merits of the old and the new cups, cells containing one of each variety were connected in series and the electrolysis conducted in the usual manner. The results are tabulated below:

	Material of cup.	Degree of porosity.	Average of resistances.	Yield of acid. Per cent.
I	Clay and sand	2.3	16.1	83.8
II	" " "	1.9	13.0	87.9
III	" " charcoal	1.4	12.9	89.4
IV	" " flint	1.3	12.8	90.7
V	Battery cup	1.0	13.2	91.4

The small yield of acid in cells Nos. I and II is probably to be ascribed, in a great measure if not altogether, to infiltration of permanganate. In general, the yield increases as the porosity diminishes. As stated elsewhere, much uncertainty attaches to the figures representing resistance. They are significant only as averages of a considerable number of observations, any one or two of which would have but little value when standing alone. Nevertheless, it is safe to conclude from the values recorded above that the more porous

cups are not to be preferred because of their smaller average resistance. As might be expected, there is a more copious deposit of oxide in their walls, in consequence of which their resistance soon becomes equal to, or even greater than, that of the less porous cups.

It is hardly necessary to add that the battery cups which were examined and used by us differed greatly among themselves in respect to porosity and resistance. Several of them were rejected because of the high resistance which they exhibited even in the fresh state.

To prepare the cups for a second experiment, they were immersed for a long time in warm, rather concentrated, hydrochloric acid, and then kept for several days under small jets of hydrant water. This treatment, when thorough, sufficed to put the cups in nearly as good condition as when new.

A 4 per cent solution of potassium permanganate would yield a very dilute solution of the acid; and, in order to obtain a more concentrated one, more of the salt must be added from time to time as the alkali is drawn into the cup and removed by the siphon. Fortunately for purposes of concentration, the electrolysis is attended in a very striking manner by the phenomenon of "electrical endosmose." With a current varying between 1 and 1.5 amperes, the water passes out of the permanganate solution into the cup; *i. e.*, in the direction of the current, at the rate of about 500 cc. per day of twenty-four hours. By replacing the water thus withdrawn from the beakers by equal volumes of the 4 per cent solution of the salt, we were able to introduce into each cell an additional 20 grams of the permanganate per day; and, accordingly, to increase the concentration of the acid to any required extent. We have not yet ascertained how far it is practicable or profitable to concentrate the acid in this manner. Up to the present time, our strongest acid has not exceeded a ten per cent solution. But apparently the limit of concentration has not been reached, since the percentage yield of the acid has not thus far shown any tendency to decline, as the strength of it increased.

Though the loss of acid during electrolysis is not relatively greater when the stronger solutions are made in the manner

described, it appears to be unprofitable to concentrate a weak acid, free from alkali, by means of the "endosmose" referred to. In one experiment in which a 3 per cent acid was concentrated to one of 7 per cent in this way, 10 per cent of the entire amount of the acid was lost; *i. e.*, reduced to oxide.

After discontinuing the addition of permanganate to replace the water drawn into the cup, two or three days are required to remove the remainder of the potassium. During this time the alkali enters the cup in constantly diminishing quantity and the endosmose becomes less and less marked. It is not necessary, however, to continue the electrolysis until no more alkali can be extracted, for a small quantity of it appears to enter the cup long after the solution without is free from potassium. This alkali is derived from the walls of the cup, where it is probably in combination with the peroxide which is always deposited to a greater or less extent both upon the surface and within the walls.

We employ the following expeditious method for determining at any time the amount of potassium still remaining in the acid, and, consequently, when to discontinue the electrolysis. A dilute filtered solution of potassium permanganate, and a dilute solution of oxalic acid *which is free from any base*, are made. It is not necessary to know the strength of either. Two equal portions of the oxalic acid are measured off and treated with equal volumes of very dilute sulphuric acid. One portion is then titrated with the solution of permanganate and the other with the filtered solution of acid which is to be tested for potassium. A drop of a neutral solution of hydrogen peroxide is added to each solution to destroy the faint rose color, and the excess of acid in both is determined by means of an alkali whose relation to the sulphuric acid is known. Or, the volumes of the permanganate and of permanganic acid which have been found equivalent, by titration against equal volumes of oxalic acid, are measured off, treated with equal volumes of the sulphuric acid, carefully reduced by a neutral solution of hydrogen peroxide, and the excess of the sulphuric acid determined as before. If the permanganic acid is free from potassium, it will, of course, on reduction, neutralize just two-thirds as much of the sulphuric acid as the

equivalent quantity of permanganate, and any additional amount which is found to have been neutralized is equivalent to the potassium still in the permanganic acid. The electrolysis has also been followed by titrating from time to time the alkali delivered by the siphons; but it is not practicable to determine, in this way, when the liquid outside of the cup is free from potassium because it is not known how much of the acid has been reduced to oxide, or how much alkali the oxide has carried down with it. In general, however, the deficit of the extracted alkali has been found to be approximately equivalent to the loss of acid.

The yield of acid has usually been from 87 to 92 per cent of the theoretically possible amount. In two cases it reached 94 per cent. The loss is due to various causes, some of which will doubtless be partially remedied after further and closer study of the conditions which control them. The greatest source of loss is the reduction of the acid to oxide, which takes place within and upon the walls of the porous cups, and also inside of them. Of the two, the former is the more serious because of its effect on the resistance of the cups. Very little oxide is found on the bottoms of the beakers when care has been taken to protect the solutions from the dust of the air. Some of the acid spatters upon the covering glasses and works its way by capillary action to the upper side, where it is reduced to oxide in contact with the air, or by the oxide previously deposited upon the glass. Another source of loss is the retention of the acid by the walls of the cups when they are removed at the close of an experiment. In two instances this was extracted and determined, and found to amount to about 3 per cent of the acid left in the beakers.

When permanganic acid is made in the manner here described, several days must elapse before a moderately concentrated solution (9 or 10 per cent) can be obtained. The last of the alkali is extracted very slowly and with a large expenditure of current. These considerations led us to try the plan of placing both electrodes in porous cups. It was foreseen that such an arrangement would give us a fairly concentrated acid within a short time, and one which would probably be free from potassium; but it appeared to be doubtful

whether the change would prove economical, inasmuch as the introduction of a second cup would increase the resistance of the cell. We have tried only one cell of this kind, but so far as we can judge from the results with it, the introduction of the second cup is advantageous. Both cups were filled with water and allowed to stand until the walls were thoroughly saturated. They were then placed in the 4 per cent solution of permanganate and the electrodes introduced. The endosmose affected only the cup containing the negative pole. Into this the water was forced at about the same rate as when one cup was used, while the level of the liquid in the acid cup remained very nearly constant. The water which passed from the outer vessel into the alkali cup was replaced, as usual, with fresh portions of the 4 per cent permanganate solution. At the end of each twenty-four-hour period, the liquid in the acid cup was withdrawn and titrated for permanganic acid and potassium, and the cup was refilled with water. This was continued for three days. The acid was found to be free from potassium and to contain no suspended oxide. The walls of the cup from which it was taken were also free from any deposit of oxide. The volume of the liquid withdrawn at the end of each day, its concentration, the weight of the acid, and also the average current are given below :

	Volume. cc.	Weight HMnO ₄ . Grams.	Concentration. Per cent.	Average current. Amperes.
1st day	235	14.280	5.95	1.44
2nd "	228	13.068	5.73	1.15
3rd "	230	16.491	7.17	1.73

The yield per ampere-hour was :

	Gram.
1st day	0.397
2nd "	0.473
3rd "	0.397
Three days	0.422

The average resistance of the cell for the three days was 14 ohms. At the close of the experiment, the free acid remaining in the liquid outside of the cups was approximately determined and found to be nearly equal to that which had entered the cup.

For purposes of comparison, we give the yield of acid per ampere-hour and the average resistance in several other experiments in which only one cup was employed :

Acid per ampere hour.		Average of resistance.	
Gram.		Ohms.	
0.332		9.6	
0.335		10.5	
0.340		9.9	
0.253		10.7	
0.266		10.0	
0.271		9.7	

A similar experiment was made on the electrolysis of a 5 per cent potassium dichromate solution in a cell with two porous cups. It was not, however, carried very far, and we have at hand only the data which were recorded during the first two days. For this time, with an average resistance of 18 ohms and an average current of 1.3 amperes, the yield was 0.551 gram of chromic acid per ampere hour. The concentration of the acid when the portions withdrawn at the end of each twenty-four hour period were mixed was 8.59 per cent. The absence of any considerable quantity of potassium was roughly demonstrated by evaporating a measured volume of the solution to dryness and heating the residue to constant weight at 150°. The weight of the residue differed only about 1 mg. from that calculated for the trioxide, CrO_3 , which had been found by titration in an equal volume of the aqueous acid.

Our work up to the present time is to be regarded as preliminary only. Much remains to be done in order to ascertain the most economical conditions of the electrolysis—how far it is profitable to concentrate the alkali around the negative, and the acid around the positive pole, the effect of temperature on the decomposition of the acid, etc. Enough has been accomplished, however, to show that the electrolytic method is a practicable one for the preparation of permanganic acid in the laboratory. Potassium permanganate is the only salt of the acid which has hitherto been available in sufficient quantities for ordinary use in the laboratory ; and this, owing to its very moderate solubility, fails often to accomplish all that could be desired of it as an oxidizing agent ; and its use involves the introduction of potassium, from which it is fre-

quently difficult to separate the products of the oxidation. Many of the other permanganates, however, like those of strontium, calcium, magnesium, zinc, and cadmium, are extremely soluble in water, and in their concentrated solutions they are violent oxidizing agents. It is to be hoped that by suitable dilution of these, any desired degree of efficiency may be secured. At 18°, the strontium salt is soluble in one-third its weight of water, giving a concentration of active oxygen in solution which has probably not been available up to the present time. The permanganates of calcium and magnesium appear to be still more soluble than that of strontium. Even the very dilute solutions of the acid act readily upon the carbonates and oxides of the metals, so that there is no difficulty in the preparation of solutions of the salts. Many of these, though not all of them, can be concentrated on the water-bath to the crystallizing-point without serious loss, provided the solutions are freed from oxide in the beginning by filtration, and are protected during evaporation from dust or other substances which can start the formation of oxide.

We are now engaged in an attempt to ascertain whether it may not be generally practicable to determine carbon in organic compounds by burning them in more or less concentrated solutions of the very soluble permanganates, and, perhaps, by use of moderate quantities of sulphuric acid, to combine the determination of nitrogen with that of carbon.

The Conductivity of Permanganic Acid.

The conductivity of permanganic acid has been determined by E. Franke¹ and J. M. Lovén.² The latter prepared his acid—which he states was free from sulphuric acid—by dissolving the anhydride in water; while that used by the former was apparently made by decomposing the barium salt with sulphuric acid. The results of the two observers appeared to differ to an extent which justified a redetermination with acid made by electrolysis. For the preparation of this we decided to electrolyze the silver, rather than the potassium, salt; because it is somewhat easier to detect a trace of silver than of potassium, and because we had observed that the acid derived

¹ Ztschr. phys. Chem., 16, 476.

² *Ibid.*, 17, 374.

from the potassium salt, when reduced and evaporated, gave in the flame a slight reaction for the metal, even when the titration showed it to be free from alkali.

In order to avoid a possible contamination of the acid through contact with glass, we substituted a large platinum dish for the beaker which was used in other experiments, making this the anode. Silver permanganate is soluble in 183 parts of water at 0°, in 107.5 at 15°, and in 59.2 at 28°.5; hence our saturated solution contained but little of the salt, and the concentration of the acid proceeded very slowly, notwithstanding the fact that the electrical endosmose is much stronger in a case of a saturated solution of silver permanganate than in that of a saturated solution of the potassium salt. The water entered the porous cup at the rate of about 50 cc. per hour, and at the end of thirty-four hours we had 4.511 grams of the acid entirely free from silver. The volume of the solution was 585 cc. This was filtered through asbestos and used in the determination of conductivity. The measurements were made at 25°. The concentration of the acid was determined with great care by means of pure potassium tetroxalate and with calibrated apparatus; the cells were standardized with a specimen of potassium chloride which had been repeatedly crystallized and frequently used for the same purpose; and, in general, every reasonable precaution was taken to insure the correctness of the results. These, it will be seen by the table given below, agree very much more closely with the results of Lovén than with those of Franke:

	M. and O.	Lovén.	Franke.
<i>v.</i>	μ_v .	μ_v .	μ_v .
2		315	
4		332	
8		348	
16	352.3	354	
32	361.2	361	
64	371.6	368	345.2
128	375.0	373	346.6
256	374.7	378	346.1
512	376.6	378	343.9
1024	377.3	376	342.8

ON CHLORINE HEPTOXIDE.

BY ARTHUR MICHAEL AND WALLACE T. CONN.

The marked increase in stability shown by non-metallic oxides and acids with increment of oxygen led us to reinvestigate perchloric acid, with a view of preparing its anhydride. For this purpose a pure acid is necessary, and as the product prepared according to the directions given by Roscoe¹ is somewhat impure, and can be obtained in this way only with a great loss of material, we modified the method by heating the perchlorate and sulphuric acid in a vacuum. Portions of 25 grams of salt and 100 grams of sulphuric acid (of about 1.839 specific gravity at 15° C.) were brought into a fractionating flask² whose low lateral tube is connected with a second flask placed in a freezing-mixture, and heated under 10-20 mm. pressure in a paraffin bath. The reaction starts at about 90° C., and perchloric acid begins to pass over when bubbles are noticeable. The heating should be gradual to prevent frothing. In about an hour the bath may be raised to 160°, and it is kept at that temperature until all the perchlorate is dissolved, the operation usually taking about two hours. It was found impossible to decompose all the perchlorate, as the process becomes reversible towards the end, and 1.5-2 grams of salt are easily regained from the cooled contents of the flask. The crude acid contained traces of sulphuric and hydrated perchloric acids, which were removed by a subsequent fractionation of the freshly prepared substance in a vacuum. The yield was 85-90 per cent of the theory, if allowance was made for the regained salt.

The acid was usually very slightly colored and differed in some of its properties from the substance described by Roscoe. Under 11 mm. pressure its vapor heated a thermometer to 19° C. In a glass-stoppered bottle the colorless oil colored on standing, even when kept from light, and after three weeks

¹ J. Chem. Soc., 16, 82.

² The neck of the flask was contracted and the air-tube fitted in tightly by means of asbestos paper, which was covered by a piece of rubber tubing; a similar joint was used between this flask and the receiver. Attached to the air-tube was a P₂O₅ drying-tube, and between the receiver and manometer a calcium soda lime tube.

was quite dark, but this sample did not explode, although it was kept several months. In contact with paper or wood it exploded with a slight blue flame, carbonizing but not igniting the material. In small amounts it could be mixed with well-cooled absolute alcohol without explosion, apparently with ester-formation, as was also the case when dry ether was used. To 5 grams dry benzene, placed in a freezing-mixture, 1 gram acid was added and the cooled tube sealed. The acid dissolved, forming a green solution, which soon deposited a carbonaceous substance, increasing in amount until the green color disappeared. The tube opened under slight pressure and no free acid could be detected in the solution. Iodine dissolved in the well-cooled acid, using the proportion of 0.5 atom to 1 molecule, to form a dark solution, which, exposed to bright light, gradually changed into an almost white substance. The tube opened under slight pressure, and the gas contained a little chlorine. On heating the substance gave off iodine, leaving a white body, which, after dissolving in water, showed tests for iodic acid.¹

The most interesting behavior of perchloric acid is towards phosphorus pentoxide, and to perform this experiment successfully it is necessary to adhere strictly to the following directions: In a small, glass-stoppered retort, connected with a drying-tube filled with phosphorus pentoxide and placed in a freezing-mixture of ice and salt, 10 grams of phosphorus pentoxide are brought and, by means of a long tube which is bent inward and contracted at the delivering end and has a rubber ball attached to the other end, not more than 10 drops of perchloric acid are added, waiting ten minutes before adding a second portion. It is advisable to allow the acid to drop on the sides of the retort, and the temperature of the freezing-mixture should be kept below -10°C . The retort, left in the freezing-mixture, is allowed to stand for a day, then connected with a well-cooled receiver, and slowly warmed in a water-bath to 85°C ., when the new oxide passes over. The product ob-

¹ In the last number of the *Annalen* (310, 369), which we have just received, Vorländer and von Schilling describe a similar method of preparing the acid, although their yield is not as favorable as ours. Their acid also appears to be somewhat more explosive, which may be due to their using a perchlorate not entirely free from chlorate.

tained in this way is practically pure and may be used for the experiments described below, but the freshly prepared substance may be redistilled under ordinary pressure without danger, when it passes over at 82°C . (corr.). It should be well borne in mind that, even though the above directions for preparing the crude oxide are followed, the apparatus may be virtually pulverized by a violent explosion, and that the personal precautions necessary for work of this kind must be always observed.

Chlorine heptoxide is a colorless, very volatile oil, that on standing a day begins to turn yellow, after two or three days is greenish-yellow, with the liberation of a greenish gas. In comparison with the previously known oxides of chlorine it shows a remarkable stability and, although when brought in contact with a flame, or by a sharp percussion, it explodes with great violence, it may be poured on paper, wood, or similar organic matter with impunity, the oxide simply volatilizing in the air. Brought into a well-cooled tube with some stick sulphur and the tube corked, no reaction occurred, even after standing several days; and what is a more striking evidence of its stability, it may be poured on a cooled piece of phosphorus and remain for some days without being attacked. With cold water it sinks to the bottom of the vessel and passes slowly over into perchloric acid, but in a closed vessel it requires some days' standing before the peculiar odor of the oxide has disappeared. Dry and cooled benzene dissolves the oxide, and after a short time a reaction ensues. With iodine a reaction occurs slowly in the dark, more rapidly in the light, with liberation of chlorine and formation of a white solid. This substance begins to decompose at 380°C ., forming iodine and oxygen, and apparently represents the heptoxide of iodine. Bromine, under similar conditions, is without action.¹

TUFTS COLLEGE, MASS.

¹ It is proposed to examine the behavior of concentrated solutions of chloric and bromic acids towards P_2O_5 . The stability of chlorine heptoxide may be explained on lines similar to those which I (J. prakt. Chem. [2], 60, 328) have given for carbon tetrachloride. This subject, which has a very important bearing on chemical affinity and on valency will be more fully discussed in a later paper.

A. M.

OBITUARY.

DR. GUILLAUME LOUIS JACQUES DE CHALMOT, a former contributor to this JOURNAL, died October 9, 1899. Dr. de Chalmot was born in Holland. He studied chemistry at the Realschule and afterwards at the Agricultural College at Wageningen. He then went to Germany and in 1891 he received the degree of Ph.D. from the University at Göttingen. He came to America soon thereafter, and took up research work in the laboratory of the Johns Hopkins University. In a few months he accepted a position as assistant chemist in the Agricultural Department of the State of Virginia at Richmond. In 1895 he became chemist of the Willson Aluminum Co. and took up the problem of calcium carbide and acetylene. His work was markedly successful both in the technical and purely scientific directions. At the time of his death he was general manager of the Willson Company. I. R.

NOTES.

Gadolinium.

In the Zeitschrift für anorganische Chemie, Vol. 22, Number 5, C. Benedicks presents a contribution to the knowledge of gadolinium. The author gives a brief historical sketch of this element with some remarks in regard to the doubts that have been expressed as to its elementary nature.

The oxide of gadolinium was first isolated from samarskite in 1880 by Marignac, who designated it temporarily by the letters $\gamma\alpha$. It was again obtained in pure condition in 1890 by Lecoq de Boisbaudran, who had previously, with Marignac's consent, named the element gadolinium. It was likewise obtained quite pure, in 1892, by Bittendorf during his researches upon the earths of the cerium and yttrium groups. In 1896, Demarcay obtained gadolinium nitrate from a mixture of the nitrates of gadolinium and samarium.

Some doubts have been expressed in regard to the right of gadolinium to be classed among the elements. In 1881, Delafontaine stated that Marignac's $\gamma\alpha$ was a mixture of the oxides of terbium and decipium. In 1885, Cleve showed that this position was untenable.

In 1886, from a study of the phosphorescent spectrum of gadolinium oxide, Crookes concluded that this so-called element must be regarded as consisting of at least three components. A similar statement, however, was made in regard to

yttrium, but this conclusion was proved later by Lecoq de Boisbaudran to be erroneous, he having shown that pure yttrium oxide gives no phosphorescent spectrum, but that such a spectrum is produced by the presence of a small quantity of kindred oxides. The author thinks that the same remarks can be applied to Crookes's conclusion as to gadolinium, since the manner of purifying the substance is not indicated.

In 1896, Demarcay isolated what he considered to be a new earth, designating the element Σ , and believing it to be one of the constituents of gadolinium. But the author states that the previous work of Lecoq de Boisbaudran on the spectrum of gadolinium and his own atomic weight determinations prove that the oxide of gadolinium can be obtained free from Demarcay's Σ .

The best method of preparing the oxide is as follows: The weaker bases are first removed by partial decomposition of the nitrates. The material is then subjected to fractional crystallization from concentrated nitric acid, thereupon to fractional precipitation with dilute ammonia, and afterwards to a final fractional crystallization from concentrated nitric acid. The nitrate is readily converted into the oxide.

The average of six atomic weight determinations, made by converting a weighed quantity of the oxide into the sulphate, gives for gadolinium the value 156.38. Bettendorf, who has also determined the atomic weight from very pure material, has formed for it the number 156.33.

By means of a Salet tube in connection with an induction coil with a long spiral wire, a beautiful spectrum consisting of bands and bright lines can be obtained without difficulty.

The salts are easily prepared from the oxide, which has the composition Gd_2O_3 , many of them crystallizing in forms so large and perfect as to admit of exact measurement. The following is a list of those prepared by the author:

Gadolinium chloride, $GdCl_3 + 6H_2O$.

Gadolinium bromide, $GdBr_3 + 6H_2O$.

Gadolinium platonic chloride, $GdCl_3 \cdot PtCl_3 + 10H_2O$.

Gadolinium aurichloride, $GdCl_3 \cdot AuCl_3 + 10H_2O$.

Gadolinium platinocyanide, $2Gd(CN)_3 \cdot 3Pt(CN)_4 + 18H_2O$.

Gadolinium nitrate, $Gd(NO_3)_3 + 6\frac{1}{2}H_2O$.

Gadolinium nitrate, $Gd(NO_3)_3 + 5H_2O$.

Gadolinium sulphate, $Gd_2(SO_4)_3 + 8H_2O$.

Gadolinium potassium sulphate, $Gd_2(SO_4)_3 \cdot K_2SO_4 + 2H_2O$.

Gadolinium selenate, $Gd_2(SeO_4)_3 + 10H_2O$.

Gadolinium selenate, $Gd_2(SeO_4)_3 + 8H_2O$.

Gadolinium potassium selenate, $Gd_2(SeO_4)_3 \cdot 3K_2SO_4 + 4H_2O$.

Acid gadolinium selenite, $Gd_2(SeO_3)_3 \cdot H_2SeO_3 + 6H_2O$.

Gadolinium ethylsulphate, $\text{Gd}(\text{C}_2\text{H}_5\text{SO}_4)_2 + 9\text{H}_2\text{O}$.

Gadolinium vanadate, $\text{Gd}_2\text{O}_3 \cdot 3\text{V}_2\text{O}_5 + 26\text{H}_2\text{O}$.

Basic gadolinium carbonate, $\text{Gd} \cdot \text{OH} \cdot \text{CO}_3 + \text{H}_2\text{O}$.

Neutral gadolinium carbonate, $\text{Gd}(\text{CO}_3)_2 + 13\text{H}_2\text{O}(?)$.

Gadolinium oxalate, $\text{Gd}_2(\text{C}_2\text{O}_4)_3 + 10\text{H}_2\text{O}$.

Gadolinium acetate, $\text{Gd}(\text{C}_2\text{H}_3\text{O}_2)_3 + 4\text{H}_2\text{O}$.

Gadolinium propionate, $\text{Gd}(\text{C}_3\text{H}_5\text{O}_2)_3 + 3\text{H}_2\text{O}$.

Special attention is called to the fact that the double cyanide, $2\text{Gd}(\text{CN})_3 \cdot 3\text{Pt}(\text{CN})_2 + 18\text{H}_2\text{O}$, is isomorphous with the corresponding double cyanides of yttrium and erbium, while the sulphate, $\text{Gd}_2(\text{SO}_4)_3$, is likewise isomorphous with the corresponding yttrium sulphate.

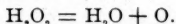
While nothing definite can be said in regard to the position of gadolinium in the periodic system, the author thinks it probable that it will find its place in the eighth horizontal series of Mendeléeff's scheme.

W. M. B.

On Inorganic Ferments.

A paper has recently appeared by G. Bredig and R. Müller von Berneck¹ under the surprising title of "Inorganic Ferments." We have hitherto been accustomed to regard fermentation as peculiar to, and produced only by, organic living matter; but these authors point out very close analogies between the action of certain inorganic substances and the organic ferments. There are many reactions effected by organic ferments, which are also brought about by finely divided metals, oxides, etc. Take the following as an example, alcohol is oxidized to acetic acid by the oxygen of the air, not only by means of the ferment *mycoderma aceti*, but also by finely divided platinum.

To discover any relations which may exist between the action of ferments and inorganic substances, it is desirable to find some reaction which is effected by both classes of substances. The reaction must then be studied in every possible manner, when brought about on the one hand by the ferment, and on the other by the inorganic substance. Such a reaction is the following:



This reaction is produced by organic ferments in general, and also by finely divided metals and oxides. The authors study this reaction in detail as it takes place in the presence of finely divided platinum. To prepare the colloidal solutions, so-called, of the metals, the older method of reducing a salt of the metal is not used, but an electrical method is em-

¹ Ztschr. phys. Chem., 31, 1258 (Jubelband für van 't Hoff).

ployed. Pseudo solutions, generally called colloidal solutions of platinum, iridium, palladium, silver and gold can be prepared by making bars of the metal the poles of a current, immersing the poles in water, and bringing them sufficiently close to produce an electric light under the water. The metal is torn off in a very fine state of division and forms a dark-brown pseudo solution in the water. A pseudo solution of platinum was thus prepared in very pure water. When examined under a high-power microscope the solution appeared perfectly homogeneous, which shows the very fine state of division of the metal. The platinum in the solution could be determined by boiling with concentrated hydrochloric acid, when it clotted and settled to the bottom.

The action of the pseudo solution of platinum, above described, on hydrogen dioxide was then studied. It was found, from the velocity of the reaction, that it is of the first order in neutral or weakly acid solution, which means that it is a monomolecular reaction. This is analogous to the action of ferments.

The second point investigated was the amount of the platinum solution required to decompose the hydrogen dioxide. It is characteristic of the action of ferments that a very small quantity is capable of bringing about a large amount of decomposition. It was found that a gram-atomic weight of platinum in 70,000,000 liters of water accelerates the decomposition of hydrogen dioxide to an appreciable extent, and can decompose, relatively, an enormous amount of the dioxide. Other inorganic substances, such as manganese dioxide and lead dioxide have the same property.

The action of ferments can be modified by change of conditions such as temperature, presence of foreign substances, etc. The action of the platinum is affected by change in temperature, by the presence of electrolytes, by the concentration of the solution, etc.

But the most striking analogy between the action of ferments and that of the platinum is the following: It is well known that a very small quantity of certain substances is capable of poisoning the organic ferments and entirely destroying their activity. The poisonous action of hydrocyanic acid and other molecules and ions, on organic ferments, have been studied quantitatively, and the most striking result is the almost infinitesimal quantity of the poison required to destroy the characteristic action of the ferment, and even the ferment itself.

It is shown by Bredig and von Berneck that the platinum solution can also be poisoned by minute traces of certain sub-

stances, so that it will no longer have the same power to decompose hydrogen dioxide. Thus, a gram-molecular weight of hydrocyanic acid in 1,000,000 liters of water will retard, quite appreciably, the decomposition of the dioxide by the platinum solution. Hydrogen sulphide acts to nearly the same extent, and mercuric chloride also shows a marked power to poison the platinum solution.

These are some of the analogies pointed out between the action of organic ferments and of the finely divided metals and oxides of the metals. It is too early to draw any final conclusion as to how deep-seated these analogies are, but they are certainly interesting and promise much for the future. Should it be shown that these relations are fundamental, it will be of service in studying the action of organic ferments in general, since the metals and even the metallic oxides are simple substances in comparison with the organic enzymes. H. C. J.

REVIEWS.

A SYSTEM OF INSTRUCTION IN QUALITATIVE CHEMICAL ANALYSIS. By ARTHUR H. ELLIOTT, PH.D., Professor Emeritus of Chemistry and Physics in the College of Pharmacy in the City of New York, and GEORGE A. FERGUSON, PH.B., Professor of Analytical Chemistry and Director of the Chemical Laboratory in the College of Pharmacy of the City of New York. Third edition, revised and enlarged. 1899. Published by the authors. 155 pp.

As the first and second editions of this book have been favorably noticed in this JOURNAL,¹ it is only necessary to say that the revision is judicious, and that the manual will be found especially useful to those teachers who are compelled to instruct large classes without assistance, as the notes of analytical details are unusually full and minute.

E. R.

DETERMINATION OF RADICLES IN CARBON COMPOUNDS. By DR. H. MEYER, Docent and Adjunct of the Imperial and Royal German University, Prague. Authorized translation. By J. BISHOP TINGLE, PH.D., F.C.S., Instructor of Chemistry at the Lewis Institute, Chicago, Ill. First Edition. First Thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1899. pp. 133.

Dr. Meyer's book is favorably known to chemists in the original and its character is such as to lead to the belief that the English translation will be of service. No doubt some of the methods described could be made part of a laboratory course in organic chemistry to the great advantage of the course, and it is to be hoped that those who have charge of the work in organic preparations in our larger laboratories will avail themselves of some of the suggestions made in the book.

There are five chapters: The first treats of the determina-

¹ Vol. 15, 373; and 16, 476.

tion of hydroxyl; the second of the determination of methoxyl, $\text{CH}_3\text{O}-$, ethoxyl, $\text{C}_2\text{H}_5\text{O}-$, and carboxyl, COOH ; the third of the determination of carbonyl; the fourth of the determination of the amino group and of the imino group; the fifth of the determination of the diazo group, of the hydrazide group, of the nitro group, of the iodoso and iodoxy groups, and of the peroxide group.

The following quotation will indicate the object of the book : "The quantitative analysis of organic compounds, as usually performed, consists almost exclusively in the determination of ions, since in the present state of the science this generally suffices for the identification of the substance; but to attain the same end in the case of organic bodies the elementary analysis requires supplementing by other methods. The percentage composition gives no information about the relative arrangement of the atoms in the molecule, but the demand for methods of analysis which will yield such knowledge increases with our growing insight into the constitution of carbon compounds. * * * The successful methods hitherto proposed for the determination of organic radicles have been collected together in this work, and it is hoped that they may serve to indicate the direction in which research may be successfully prosecuted for the discovery of new ones applicable to hitherto unforeseen conditions."

The book is recommended to teachers and advanced students of chemistry.

I. R.

ADDITIONS.

Vol. 23, pages 309, 310, and 311.

Under plate on page 309 add:

1. Metadinitrobenzene; 2. Orthonitrophenol; 3. Metamethoxybenzenesulphonamide; 4. Benzenesulphonamide; 5. Nitromethane; 6. Paramethoxybenzenesulphonamide; 7. Orthomethoxybenzenesulphonamide; 8. Trinitrotoluene.

Under plate on page 310 add:

1. Potassium Chloride; 2. Potassium Nitrate; 3. Ammonium Chloride; 4. Ammonium Nitrate; 5. Silver Iodide; 6. Strontium Nitrate.

Under plate on page 311 add:

1. Sodium Bromide; 2. Potassium Metanitrobenzenesulphonate; 3. Sodium Bromate; 4. Metanitrobenzenesulphonamide; 5. Benzoic Sulphinide.